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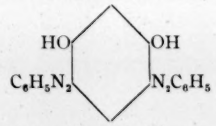
SOME DISAZO AND TRISAZO DERIVATIVES OF RESORCIN.

BY W. R. ORNDORFF AND B. J. RAY.

It is a well-known fact that the diazonium salts combine with resorcin to give two isomeric disazo compounds. One of these, known as the symmetrical resorcindisazobenzene, is formed by combining the diazonium salt with resorcin in caustic alkali solution in the proportion of two molecules of the former to one of the latter. That this substance is really the symmetrical compound,



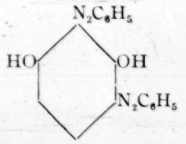
Symmetrical Resorcindisazobenzene.

follows from the work of Kostanecki,[1] who showed that it gives the symmetrical 4,6-diaminoresorcin on reduction with tin and hydrochloric acid. This symmetrical resorcindisazobenzene is identical with the α-resorcindisazobenzene

[1] Ber. d. chem. Ges., **21**, 3114.

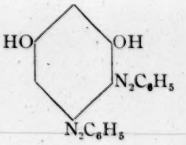
previously made by O. Wallach and B. Fischer,[1] as shown by the fact that both yield the same diacetyl compound melting at 183°–184°.

The second, or unsymmetrical, resorcindisazobenzene,



Unsymmetrical Resorcindisazobenzene.

was first obtained by Liebermann and Kostanecki[2] as a by-product in the preparation of resorcinmonazobenzene and was separated from this by means of its insolubility in dilute alkalies. As it was not identical with either the α or β compound of Wallach and Fischer, they named it γ-resorcindisazobenzene. Later, Kostanecki[3] found that it is exclusively formed when two molecules of the diazonium salt and one of resorcin are combined in the presence of sodium acetate or sodium carbonate solutions. It yields a diacetyl compound which melts at 137°–138° and differs in other respects from the symmetrical product. That it has the unsymmetrical structure represented by the above formula was proven by the fact that on reduction with tin and hydrochloric acid it gives the unsymmetrical 2,4-diaminoresorcin.[4] The only other theoretically possible formula for a resorcindisazobenzene,

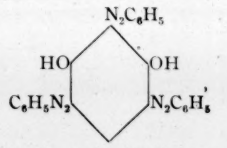


has an azo group in the meta position to both hydroxyl groups,

[1] Ber. d. chem. Ges., **15**, 2814.
[2] *Ibid.*, **17**, 880.
[3] *Ibid.*, **21**, 3114.
[4] *Ibid.*, **17**, 880.

which Kostanecki[1] thinks is very improbable, since there are both an ortho and a para position free. In a footnote he suggests this formula for the β-resorcindisazobenzene of Wallach and Fischer, which is formed only in very small quantity, together with the symmetrical compound, when a caustic potash solution of the monazo product is treated with a diazonium salt. He is careful to point out, however, that, as the reduction products of this β compound are not known, this structural formula has no valid basis.

If the two structural formulas given above for the symmetrical and the unsymmetrical resorcindisazobenzenes be examined, it will be seen that in the symmetrical compound both azo groups have entered the molecule in the para position to one of the hydroxyl groups and ortho to the other, while in the unsymmetrical product only one of the azo groups is para to one of the hydroxyl groups and ortho to the other, the second azo group having taken the position ortho to both of the hydroxyl groups. In other words, *in each compound there is a position vacant which is occupied by an azo group in the other.* It seemed highly probable, therefore, that it would be possible to introduce azo groups into these unoccupied positions and thus make trisazo compounds of resorcin. Furthermore, both of the above disazo compounds should yield the same trisazo product when treated with benzenediazonium chloride,



Resorcin-2,4,6,-trisazobenzene.

and the positions of the azo groups would thus be determined as 2, 4 and 6, since in the symmetrical product the azo groups are known to be in positions 4 and 6 and in the unsymmetrical compound in 2 and 4. There was also the possibility that

[1] Ber. d. chem. Ges., **21**, 3114.

the β-resorcindisazobenzene of Wallach and Fischer might be the above trisazo compound, as it was made by the action of benzenediazonium chloride on a solution of resorcinmonazobenzene in caustic potash, and there seems to be no reason why the symmetrical disazo compound, which is formed here in much larger quantity and is soluble in caustic potash solution, should not be, partly at least, converted into the trisazo product by the diazonium salt.

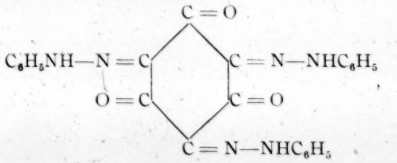
Following out this line of reasoning, we made the above trisazo compound from both the symmetrical and unsymmetrical disazo product, as well as from benzenediazonium chloride and resorcin by combining them in the proportion of three molecules of the former to one of the latter. After we had completed this work and were making other trisazo compounds of resorcin, the article on phenol-2,4,6-trisazobenzene, by E. Grandmougin and H. Freimann, appeared.[1] This caused us to publish a short preliminary paper on resorcin-2,4,6-trisazobenzene in the same journal.[2]

About this time, also, we found in the article of Wallach and Fischer[3] the following statement, which had previously escaped us and also, apparently, Grandmougin and Freimann, as they make no mention of it: "Wir haben uns endlich davon überzeugt dass die *Disazoverbindungen sich sehr leicht in Trisazoverbindungen überführen lassen,* indem man die α-Disazoverbindungen in alkalischer Lösung mit Diazoverbindungen umsetzt. Diese Trisazoverbindungen sind aber bisher noch nicht näher untersucht." It seems very remarkable, in view of this statement, that Wallach and Fischer never even suspected that their β-resorcindisazobenzene, which was made by treating the monazo compound dissolved in strong caustic potash solution with benzenediazonium chloride, was in reality nothing but an impure trisazo compound.

The only other mention in the literature of trisazo compounds of this type, in which all of the azo groups are connected with the same benzene residue, is found in an article published

[1] Ber. d. chem. Ges., **40**, 2662 (1907).
[2] *Ibid.*, **40**, 3212 (1907).
[3] *Ibid.*, **15**, 2814.

in 1897 by A. G. Perkin[1] on phloroglucinoltrisazobenzene. This compound was made by adding an excess of a solution of benzenediazonium sulphate to a solution of phloroglucinol in dilute sodium carbonate solution. Perkin found that the formation of this trisazo product was not dependent on the amount of the diazonium salt present, as the same trisazo compound was always formed even if the disazonium salt were present in the proportion of one or two molecules to one molecule of the phloroglucinol, part of the phloroglucinol being unacted on in this case. He regards the substance as having the following structure,



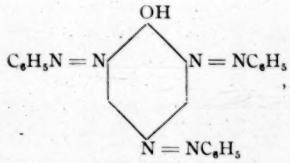
Phloroglucinoltrisazobenzene.

since "it is insoluble in cold alkali solutions and contains no hydroxyl groups, those originally present in the phloroglucinol having assumed the ketonic form from their ortho position relatively to the azo groups." This trisazo compound dissolves in concentrated sulphuric acid with a deep crimson coloration and, as was to be expected, it also results from the action of diazobenzene sulphate on an alkaline solution of phloroglucinoldisazobenzene.

Grandmougin and Freimann state that phenol-2,4,6-trisazobenzene is formed, together with phenoldisazobenzene, when three molecules of diazonium chloride act on phenol in caustic alkaline solution, and they emphasize the fact that their trisazo compounds were formed only in the presence of caustic alkalies, while in the case of monazo compounds it is a matter of indifference whether the combination be brought about with caustic alkalies or with the alkaline carbonates or acetates. In the formation of the disazo compounds of phenol, however, the presence of acetate is unfavorable to

[1] J. Chem. Soc., **71**, 1154.

the reaction, which takes place readily in solutions of the alkaline carbonates or hydroxides. In the latter case some trisazo product may also be formed as a by-product. They give the following formula to their phenoltrisazobenzene,



Phenol-2,4,6,-trisazobenzene.

since, on reduction with tin and hydrochloric acid, it gives 2,4,6-triaminophenol identical with the reduction product of picric acid.

Freimann[1] gives the following generalizations in regard to the color of the azo compounds of phenol when dissolved in concentrated sulphuric acid: the monazo compounds dissolve in concentrated sulphuric acid with a pure yellow color, which remains yellow on dilution, the disazo products with a yellowish-orange color, which becomes red to dirty reddish-violet on dilution and the trisazo compounds dissolve in the same solvent with a deep reddish-violet color and are precipitated out on dilution. It will be seen that the trisazo compounds of phloroglucinol prepared by Perkin differ from the trisazo compounds of phenol in two respects. In the first place they are formed in the presence of sodium carbonate, caustic alkalies not being essential for their formation, and in the second place they dissolve in concentrated sulphuric acid with a deep crimson color.

In regard to the position and number of the azo groups which enter the phenol molecule, three cases have been distinguished up to the present time:[2]

1. If equimolecular quantities of the phenol and the diazonium salt react there is formed:

[1] Zur Kenntnis der Azo-Derivate des Phenols und der Phenolcarbonsäuren; Diss. Zürich, 1908.

[2] V. Meyer and P. Jacobson: Lehrbuch d. org. Chemie, II, 1, 397.

(*a*) From a phenol in which the para position to the hydroxyl group is unoccupied, a *para*hydroxyazo compound.

(*b*) From a phenol whose para position to the hydroxyl group is occupied, but whose ortho position is free, an *ortho*-hydroxyazo compound.

2. If two molecules of the diazonium salt react with one molecule of the phenol there is formed a hydroxy*dis*azo compound, when the para position to the hydroxyl group in the phenol and at least one ortho position are free. These disazo products are also formed as by-products when equimolecular quantities react.

It has also been found that *p*-hydroxybenzoic acid reacts with diazonium salts, yielding the same products as phenol itself, owing to the elimination of carbon dioxide.[1] This is true also for the trisazo compounds, as Grandmougin and Freimann found that the product, melting at 213°–215°, first prepared by Limpricht and Fitze[2] by the action of benzenediazonium chloride on *p*-hydroxybenzoic acid, was phenol-2,4,6-trisazobenzene. They also found that a small amount of the azo derivative of the carbonic acid is formed here.

For case (1*a*) the following exceptions have been observed: *o*-Hydroxyazo compounds are formed, together with the *p*-hydroxyazo products, even when the para position to the hydroxyl group is free. Thus, in the action of diazotized nitrotoluidine on nitrocresol, *o*-azonitrotoluenenitrocresol is formed as well as the para product,[3] and in the direct combination of a diazonium salt with phenol there is formed, in addition to the main product, *p*-hydroxyazobenzene, the ortho compound to the extent of one per cent. of the weight of the aniline used.[4] Further, exceptions are also known in the naphthalene series; for example, the formation of *o*- and *p*-nitrobenzeneazo-2-α-naphthol in addition to the 4-azo derivative[5],

[1] Limpricht: Ann. Chem. (Liebig), **263**, 236. See also Grandmougin and Freimann: Ber. d. chem. Ges., **40**, 3453.

[2] Ann. Chem. (Liebig), **263**, 236.

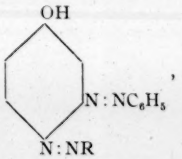
[3] Michel and Grandmougin: Ber. d. chem. Ges., **26**, 2353.

[4] Bamberger: *Ibid.*, **33**, 3188.

[5] Bamberger and Meimberg: *Ibid.*, **28**, 1889. Bamberger: *Ibid.*, **28**, 848.

and, according to a recent patent,[1] in the combination of diazo solutions (in the patent, *m*-hydroxy-*p*-diazoazobenzenesulphonic acid) with α-naphthol in extremely concentrated solutions of caustic alkali the azo group enters the ortho position.

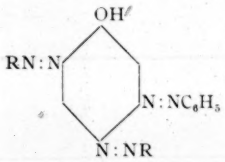
It has not been possible, hitherto, to introduce more than two azo groups into the molecule of a monacid phenol or two azo residues into the ortho positions to the hydroxyl group. The work of Grandmougin and Freimann shows that with the introduction of two azo groups the limit of combination of phenol with diazonium salts is not yet attained and also that it is possible to introduce an azo group into both ortho positions to the hydroxyl group in a monacid phenol. Our work with the diacid phenol, resorcin, and the work of Perkin with the triacid phenol, phloroglucinol, shows that trisazo compounds, in which two of the azo groups are ortho and the other para to one of the hydroxyl groups, can be made with the greatest ease. Few attempts to make trisazo compounds are to be found in the literature. Besides the statement of Wallach and Fischer, mentioned above, and the trisazo compounds of phloroglucinol also noted, Jacobson and Hönigsberger[2] obtained, by combining *m*-hydroxyazobenzene with a diazonium salt, a phenoldisazo compound, to which they give the formula



and they also consider the possibility of the formation of a trisazo product having the formula

[1] D. R. P. 14,443 (J. R. Geigy & Co.) Pat. Schriftensammlung der Chem. Z., No. 592 (1908).

[2] Ber. d. chem. Ges., **36**, 4093.



but they seem to have made no attempts to prepare this substance. If this trisazo compound can be made, there seems to be no reason why it would not be possible to introduce still another azo group into it in the position ortho to the hydroxyl group and thus make a tetrazo compound.

In the year 1904 Vignon[1] attempted to prepare the simplest trisazo compound, phenol-2,4,6-trisazobenzene, both by the action of three molecules of benzenediazonium chloride on one molecule of phenol and also by the action of one and two molecules of the diazonium chloride on hydroxyazobenzene and on phenoldisazobenzene in caustic alkaline solution. Curiously enough, he did not succeed in going beyond the disazo stage and he therefore designates the phenol*di*sazobenzene as the limit of combination of phenol with diazonium salts. In the year 1907, however, Toniolo made the observation that when two molecules of benzenediazonium chloride acted on an alkaline solution of one molecule of phenol, there was formed, in addition to the well-known 2,4-phenoldisazobenzene, a new compound in small amount. This compound had a much higher melting point than the disazo product and differed from it also in chemical properties and hence it was thought to be the phenol-2,4,6-trisazobenzene[2] which Vignon had failed to get. The investigation was then taken up by Grandmougin and Freimann, who showed that the product was really the above trisazo compound and that, contrary to the statement of Vignon, it could be obtained very readily and in considerable quantity when three molecules of the benzenediazonium chloride were allowed to act on one molecule of phenol in caustic alkaline solution.

[1] Compt. Rend., **138,** 1279.
[2] Grandmougin and Freimann: Ber. d. chem. Ges., **40,** 2662.

A great deal of work has been done of late years on the constitution of the hydroxyazo compounds, but it is impossible to review that work here. According to Auwers, who has devoted most time to this problem, these substances are all true azo compounds.[1] We shall therefore use the azo formulas in this article for all the azo compounds made by us.

EXPERIMENTAL.

Resorcintrisazobenzene.

As was stated above, it seemed likely that resorcin*tris*azobenzene would be formed if resorcin were treated with an excess of benzenediazonium chloride in caustic alkaline solution. The formation of such a compound was readily accomplished, the materials being used in the following proportions:

Resorcin (1 molecule), 11 grams; aniline (3 molecules), 27.9 grams; sodium nitrite (3 molecules), 20.7 grams; hydrochloric acid (7 molecules), 25.5 grams; sodium hydroxide (5 molecules), 20 grams.

The aniline, which was freshly distilled and pure, was dissolved in 500 cc. of dilute hydrochloric acid (sp. gr. 1.026), the solution cooled to 0° and stirred vigorously with a mechanical stirrer, while the nitrite, dissolved in 150 cc. of distilled water, was slowly added. The mixture was then stirred for twenty minutes, the temperature being kept at 0° to 5°. At the end of this time a trace of nitrous acid was still present, as shown by the reaction with starch-iodide paper.

The resorcin, dissolved in 100 cc. of distilled water, was added to the solution of the diazonium salt, the mixture stirred for ten minutes, and then poured slowly and with constant stirring into a large vessel containing the caustic soda dissolved in two liters of water and cooled down to about 0° with ice, a rise in temperature being prevented by the addition of ice from time to time.

The solution turned dark brown at once and a voluminous precipitate gradually formed. This mixture was then stirred for two days without further addition of ice and the dark brown

[1] Ann. Chem. (Liebig), **360**, 11.

precipitate filtered off and thoroughly washed with water. The filtrate contained a small amount of resorcindisazobenzene, which was thrown down as a yellowish-brown precipitate on adding an excess of acid. The dark brown product was removed from the filter, treated with dilute hydrochloric acid, washed thoroughly with water, filtered off and dried. It was then repeatedly crystallized from a mixture of chloroform and alcohol, from benzene and again from chloroform until the melting point was constant. The product thus obtained consisted of brown cigar-shaped microscopic needles, which melted sharply at 254° (uncor.[1]).

Analyses of this product, dried in the water oven at about 100° to constant weight, gave the following results:

I. 0.5990 gram substance gave 1.4955 grams CO_2 and 0.2366 gram H_2O.

0.1350 gram substance gave 24.55 cc. N (743.6 mm.[2] and 21° C.).[3]

II. 0.2157 gram substance gave 0.5391 gram CO_2 and 0.0868 gram H_2O.

0.4266 gram substance gave 74.3 cc. N (754 mm. and 15° C.).

	Calculated for $C_{24}H_{18}O_2N_6$.[4]	Found. I.	II.
C	68.21	68.08	68.16
H	4.30	4.42	4.51
N	19.91	20.08[5]	20.08

From these analyses there can be no doubt that the substance is resorcin*tris*azobenzene, $C_6H(OH)_2(N_2C_6H_5)_3$.

It is soluble in benzene, toluene and xylene, in chloroform, ethyl acetate and glacial acetic acid, but only very slightly soluble in ether and in alcohol. It dissolves in an alcoholic

[1] The melting points given in this paper were taken with a thermometer compared with one standardized by the Physikalisch-Technische Reichsanstalt.

[2] The barometer used in all our determinations had a brass scale.

[3] This analysis was made for us by Mr. E. H. Nichols.

[4] International atomic weights for 1910 are used in all calculations in this paper.

[5] In calculating the percentage of nitrogen from the volume we used 1.2507 grams as the value for the weight of a liter of nitrogen, under standard conditions, given by Guye in the J. Chim. Phys., **5**, 218 (1907), and based on the results of Rayleigh, Ramsay and Gray. Professor F. W. Clarke, of the U. S. Geological Survey, has recalculated the value of the weight of a normal liter of nitrogen (0° C. and 760 mm. at sea level and 45° latitude) as 1.25066 grams, which is essentially that of Guye.

solution of the caustic alkalies with a reddish-brown color and in concentrated sulphuric acid it gives a deep bluish-violet solution.

The crystals from chloroform and alcohol were examined by Professor A. C. Gill, of the Mineralogical Department of Cornell University, who reports as follows: "The substance crystallizes in monoclinic or triclinic needles with strong pleochroism and an extinction angle of 25° to 30° as a maximum. The color of the small needles is light yellow to deep brownish-yellow in transmitted light, becoming so dark as to seem almost black when the stage of the microscope is turned."

Diacetyl Derivative of Resorcintrisazobenzene.—For the preparation of this compound, 1.3 grams of the pure resorcintrisazobenzene were boiled for thirty minutes with an equal weight of anhydrous sodium acetate and 15 grams of pure acetic anhydride in a flask provided with a return condenser. When cold, the mixture was poured into a saturated salt solution. The resulting oil soon solidified to a yellow crystalline mass, which was washed thoroughly with water and dried. It was then recrystallized from alcohol and from a mixture of alcohol and ethyl acetate until the melting point became constant. The compound thus obtained consisted of a mass of very fine golden yellow needles, which melted sharply at 201° (uncor.). Slow crystallization from ethyl acetate or from ether gave red pyramidal crystals which melted at 203° (uncor.). These red crystals are converted into the golden yellow needles on dissolving them in alcohol and quickly cooling the saturated solution. When the yellow needles are suspended n ether they are rapidly converted into the red pyramidal crystals, this change taking place more rapidly when the ether is boiled.

Analyses of the golden yellow needles gave the following results:

I. 0.1054 gram substance gave 0.2561 gram CO_2 and 0.0440 gram H_2O.

II. 0.1376 gram substance gave 0.3344 gram CO_2 and 0.0577 gram H_2O.

0.1982 gram substance gave 30.2 cc. N (735 mm. and 23°).

	Calculated for $C_{28}H_{22}O_4N_6$.	Found. I.	II.
C	66.38	66.27	66.28
H	4.38	4.68	4.53
N	16.61	...	16.45

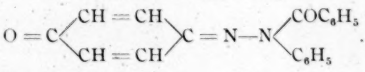
The compound is therefore the diacetyl derivative of resorcintrisazobenzene, $C_6H(OCOCH_3)_2(N_2C_6H_5)_3$. Professor Gill examined both the yellow and the red modifications of the diacetylresorcintrisazobenzene and found that the former crystallized in "yellow, very slightly pleochroic needles, with parallel or nearly parallel extinction, optically biaxial, positive, with the plane of the optical axes across the needles, and an optical angle of about 70°. They are probably monoclinic. The needles are about 0.01 mm. by 1 or 1.5 mm. in size."

In the case of the latter modification he states: "the brilliant red crystals show much variation in habitus, from tabular to stout columnar, to pyramidal. The tabular crystals are six-sided, and at first sight look as if monoclinic with the clinopinacoid as the principal face, the other boundaries being in the position of base, orthopinacoid and prism. They show oblique extinction, but also an obtuse bisectrix obliquely inclined to the large face, hence the crystallization is doubtless triclinic. Pleochroism is very marked, from clear yellow to deep red, and the double refraction is above 0.05."

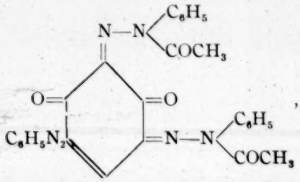
In order to determine which of the two forms of the diacetyl derivative is the more stable, the golden yellow needles were dissolved in absolute alcohol and the solution concentrated until it was saturated. A few of the red pyramidal crystals were then added and the solution allowed to cool very slowly. The resulting crystals consisted entirely of the red pyramidal form. This experiment was repeated, with acetic acid and then benzene as solvents, and only the red pyramidal crystals were obtained. Further work showed that the golden yellow needles are obtained only under special conditions, *viz.*, by quick cooling of a saturated solution or by precipitation with some solvent in which the compound is but slightly soluble. The red pyramidal crystals are therefore the stable form. The yellow needles do not contain any solvent of crystallization, such as alcohol or water, as was determined by

heating them in a Victor Meyer air bath to 110° for one hour. The loss in weight was only 0.12 per cent. The analyses of the compound also showed that it contained no solvent. Later the red pyramidal crystals were also analyzed and found to contain no solvent.[1]

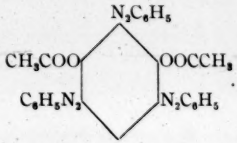
This conduct of the diacetylresorcintrisazobenzene is very similar to that of the quinonebenzoylphenylhydrazone made from quinone and benzoylphenylhydrazine:



McPherson[2] describes two crystal forms of this substance and Willstätter and Veraguth[3] add that it is dimorphous, forming light yellow prisms, which go over into reddish-yellow rhombohedra (almost cubical crystals) on covering them with ether or on heating them to about 100°, and slowly even on standing. This similarity in conduct might be used as an argument in favor of the quinonephenylhydrazone formula for the diacetylresorcintrisazobenzene,



instead of the one which would naturally be given to the substance:



[1] See page 19.
[2] This Journal, **22**, 364 (1899).
[3] Ber. d. chem. Ges., **40**, 1434 (1907).

Now Willstätter and Veraguth[1] have shown that quinonebenzoylphenylhydrazone is readily transformed into benzoylhydroxyazobenzene by simply shaking the dry ethereal solution with pulverized caustic potash, the benzoyl group migrating from the nitrogen to the oxygen atom according to the scheme,

$$C_6H_5N(COC_6H_5)—N=C_6H_4=O \longrightarrow C_6H_5N=N—C_6H_4—OCOC_6H_5;$$

and we thought that if our diacetyl derivative were a quinonephenylhydrazone it might act in a similar manner. On shaking it in solution in anhydrous ether with dry powdered caustic potash, however, even at 0°, the color of the solution changed from yellow to red and the solid alkali turned black. After five minutes the ether was removed and evaporated, the residue treated with dilute hydrochloric acid, and the resulting reddish-brown powder washed with water and dried. When crystallized from ethyl acetate it melted at 254° (uncor.), showing that the diacetyl derivative was saponified by this process, yielding the free trisazo compound.

It is impossible, therefore, to say whether the two forms of diacetylresorcintrisazobenzene represent stereoisomeric quinonephenylhydrazones or are simply two crystal modifications of the same substance. Possibly the isomerism may be similar to that suggested by Hantzsch and Robertson[2] to explain the yellow and red forms of the salts and hydrates of the hydroxyazo compound. They obtained the silver salt of hydroxyazobenzene almost always in a red modification, which was, however, so unstable that it changed into the yellow form even under the solution.

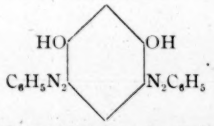
Preparation of Resorcintrisazobenzene from the Symmetrical and the Unsymmetrical Resorcindisazobenzene.

In order to determine the positions of the azo groups in the molecule of resorcintrisazobenzene, this compound was made from both the symmetrical and unsymmetrical resor-

[1] Ber. d. chem. Ges., **40**, 1434 (1907).
[2] *Ibid.*, **43**, 106 (1910).

cindisazobenzenes and the products compared with each other and with that made from three molecules of the diazonium salt and one of resorcin.[1] The two resorcindisazobenzenes were prepared according to the directions of Kostanecki.[2]

Symmetrical Resorcindisazobenzene,



—In the preparation of this product the materials were used in the following proportions:

Resorcin (1 mol.), 22.0 grams; aniline (2 mols.), 37.2 grams; hydrochloric acid (5 mols.), 36.5 grams; sodium nitrite (2 mols.), 27.6 grams; sodium hydroxide (4 mols.), 32.0 grams.

The pure aniline was dissolved in 500 cc. of dilute hydrochloric acid (sp. gr. 1.0345) and the solution cooled with ice and stirred vigorously with a mechanical stirrer, while the nitrite, dissolved in 100 cc. of distilled water, was slowly added. After twenty minutes a slight excess of nitrous acid was shown to be present by means of starch-iodide paper. The resorcin, dissolved in 500 cc. of distilled water and cooled to 0°, was then added, the mixture stirred for ten minutes, and then poured slowly and with constant stirring into the caustic alkali dissolved in two liters of ice water. The solution turned deep red and a small amount of a dark precipitate separated. This mixture was stirred for twenty-four hours and allowed to warm up to room temperature gradually. The precipitate was then filtered off and the filtrate acidified. The voluminous yellowish-brown precipitate was washed with water till free from salts and then dried. After crystallization from chloroform and alcohol it melted sharply at 217° (uncor.) and corresponded in every respect with the description of the symmetrical resorcindisazobenzene given in the literature. It is soluble in chloroform, benzene, toluene, xylene, ethyl acetate and glacial acetic acid, slightly soluble

[1] See page 11.

[2] Ber. d. chem. Ges., **21**, 3117.

in alcohol, while it is almost insoluble in ether. Aqueous caustic alkalies dissolve it very readily and it is also taken up by concentrated sulphuric acid, forming a rose-colored solution.

Diacetyl Derivative of Symmetrical Resorcindisazobenzene.—This product was made in the same manner as the diacetylresorcintrisazobenzene. It was crystallized from alcohol and then from ethyl acetate until the melting point became constant. The light yellow needles thus obtained melted sharply at 183° (uncor.) and gave the following result on analysis:

0.1736 gram substance gave 0.4179 gram CO_2 and 0.0721 gram H_2O.

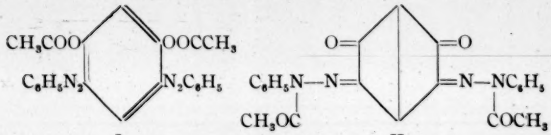
	Calculated for $C_{22}H_{18}O_4N_4$.	Found.
C	65.65	65.65
H	4.50	4.65

The compound was therefore the diacetyl derivative of the symmetrical resorcindisazobenzene,

$$C_6H_2(OCOCH_3)_2(N_2C_6H_5)_2.$$

It is soluble in ethyl acetate, benzene, toluene, acetic acid, ether, alcohol and acetone. The crystals from ethyl acetate were examined by Professor Gill, who reports as follows: "The four-sided, needle-shaped crystals show only very slight pleochroism. They have a yellow color and an extinction angle of 0° to 15°. The double refraction is medium strong, plane of the optical axes across the direction of elongation and the optical character is positive. The system is probably monoclinic, the prisms being terminated by a clinodome which makes an angle of about 25° with the base. The base, however, is not developed and the angle was measured on a microscope stage and is only approximately correct."

Two structural formulas are possible for this substance:



I. II.

Diacetylresorcindisazobenzene.

According as it is regarded as a true azo compound (I) or as

a quinone phenylhydrazone derivative (II). In order to determine which of these formulas is correct, the substance was treated with phenylhydrazine in alcoholic solution and also in acetic acid. In all cases the diacetyl product was saponified with the formation of the resorcindisazobenzene.

Resorcintrisazobenzene from the Symmetrical Resorcindisazobenzene.—In the preparation of the trisazo compound from the symmetrical resorcindisazobenzene the materials were used in the following proportions:

Symmetrical resorcindisazobenzene (1 mol.), 31.8 grams; sodium hydroxide (5 mols.), 20.0 grams; aniline (1 mol.), 9.3 grams; sodium nitrite (1 mol)., 6.9 grams; hydrochloric acid (3 mols.), 11.0 grams.

The disazo compound was placed in a large cylinder and the caustic soda dissolved in two liters of water poured over it, the mixture being stirred until complete solution took place, and then it was cooled by adding ice. In the meantime the aniline was dissolved in one liter of hydrochloric acid (sp. gr. 1.005) and converted into the diazonium salt in the usual way. This solution was then added slowly and with vigorous stirring to the ice-cold solution of the disazo compound in caustic soda. The deep red solution immediately turned dark brown and a heavy precipitate was formed. The mixture was stirred for twenty-four hours and allowed to warm up to room temperature gradually. The dark brown precipitate was then filtered off, washed with water, suspended in dilute hydrochloric acid, again filtered, washed and dried. After several crystallizations from a mixture of chloroform and alcohol and from benzene it melted sharply at 254° (uncor.) and had all the other properties characteristic of the trisazo compound already described. After drying in the water oven to constant weight it was analyzed:

I. 0.2259 gram substance gave 0.5644 gram CO_2 and 0.0885 gram H_2O.

II. 0.2241 gram substance gave 0.5604 gram CO_2 and 0.0851 gram H_2O.

0.3081 gram substance gave 56.3 cc. N (737 mm. and 23°).

	Calculated for $C_{24}H_{18}O_2N_6$.	Found. I.	II.
C	68.21	68.14	68.20
H	4.30	4.39	4.25
N	19.91	...	19.78

The substance is therefore resorcintrisazobenzene,

$$C_6H(OH)_2(N_2C_6H_5)_3,$$

and is identical with the product made by the action of three molecules of the diazonium salt on an alkaline solution of resorcin.

Diacetyl Derivative of Resorcintrisazobenzene Made from the Symmetrical Disazo Compound.—This product was made by the method already described. The two modifications, yellow needles melting at 201° and red pyramidal crystals melting at 203°, were obtained and shown to correspond in all respects to the diacetyl derivative made from the resorcintrisazobenzene obtained from resorcin by combining it with three molecules of the diazonium salt.

Analyses of the yellow needles (I) and of the red pyramidal crystals (II) show that these two forms have the same chemical composition:

I. 0.17405 gram substance gave 0.4231 gram CO_2 and 0.0698 gram H_2O.

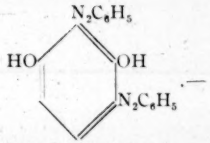
II. 0.3854 gram substance gave 0.9386 gram CO_2 and 0.1523 gram H_2O.

0.2746 gram substance gave 41.6 cc. N (743 mm. and 21°).

	Calculated for $C_{28}H_{22}O_4N_6$.	Found. I.	II.
C	66.38	66.30	66.42
H	4.38	4.49	4.43
N	16.61	...	16.71

When this diacetyl derivative is treated with phenylhydrazine at room temperature and the mixture is allowed to stand, it gradually warms up and an exceedingly vigorous reaction takes place, accompanied by charring and the formation of tarry substances.

Unsymmetrical Resorcindisazobenzene,



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The materials were used in the following proportions:

Resorcin (1 mol.), 22.0 grams; aniline (2 mols.), 37.2 grams; sodium nitrite (2 mols.), 27.6 grams; hydrochloric acid (5 mols.), 36.5 grams; sodium acetate (4 mols.), 65.6 grams.

The solution of the diazonium salt was prepared in the usual way, using 500 cc. of hydrochloric acid (sp. gr. 1.0345). The mixture of the diazonium salt and resorcin was poured slowly and with constant stirring into the sodium acetate dissolved in two liters of ice water. After stirring for two days the red precipitate was washed thoroughly by decantation, filtered off and dried. Crystallized from a mixture of chloroform and alcohol, the compound melted at 221° (uncor.) and corresponded in all other respects to the unsymmetrical resorcindisazobenzene described in the literature.

An analysis gave the following result:

0.1992 gram substance gave 0.4963 gram CO_2 and 0.0844 gram H_2O.

	Calculated for $C_{18}H_{14}O_2N_4$.	Found.
C	67.90	67.94
H	4.43	4.75

Professor Gill describes the crystals as "reddish needles with parallel extinction, strong double refraction and weak pleochroism. Absorption rather strong but yellow in *thin* layers made by rubbing with the finger nail."

Diacetyl Derivative of Unsymmetrical Resorcindisazobenzene.—This substance was prepared in the usual way. It crystallized from alcohol in yellow needles which melted sharply at 137° (uncor.). An analysis resulted as follows:

0.2336 gram substance gave 0.5610 gram CO_2 and 0.0973 gram H_2O.

	Calculated for $C_{29}H_{18}O_4N_4$.	Found.
C	65.65	65.50
H	4.50	4.66

According to Professor Gill, the "masses of extremely fine capillary crystals show parallel, or nearly parallel, extinction and slight pleochroism, the greater absorption being across the elongation of the needles." This diacetyl compound also reacts with phenylhydrazine in glacial acetic acid solution but no definite product could be isolated from the tarry residue obtained.

Resorcintrisazobenzene from the Unsymmetrical Resorcindisazobenzene.—The materials were used in the following proportions:

Unsymmetrical resorcindisazobenzene (1 mol.), 31.8 grams; sodium hydroxide (5 mols.), 20.0 grams; aniline (1 mol), 9.3 grams; sodium nitrite (1 mol.), 6.9 grams; hydrochloric acid (3 mol.), 11.0 grams.

The disazo compound was placed in a large glass cylinder with the alkali dissolved in four liters of water, and complete solution effected by passing in steam. The solution of the diazonium salt was then prepared by the method already given and added slowly and with constant stirring to the ice-cold alkaline solution of the disazo compound. The solution turned darker immediately and a heavy precipitate separated. This mixture was stirred for two days without further addition of ice. The precipitate was filtered off, washed thoroughly with water, suspended in dilute hydrochloric acid, washed, filtered and dried. On recrystallization from chloroform and alcohol and from benzene until the melting point became constant, the product was found to be identical with the trisazo compound prepared by the two methods already described.

A much purer product was obtained by dissolving the disazo compound in an alcoholic solution of caustic soda and then adding an aqueous solution of the diazonium salt. The aqueous solution of benzenediazonium chloride, prepared from 1.55 grams of aniline, 1.15 grams of sodium nitrite,

and 160 cc. of hydrochloric acid (sp. gr. 1.005), was added slowly and with constant stirring to an ice-cold solution of 5 grams of caustic soda and 5.3 grams of the disazo compound in two liters of absolute alcohol. The mixture was constantly stirred for 24 hours and allowed to warm up to room temperature gradually. Most of the trisazo compound remained in solution, but on acidifying fine reddish-brown needles were precipitated. Crystallization from benzene gave small, light brown, cigar-shaped needles, which melted sharply at 254° (uncor.). Analyses of the two products gave the following results:

I. 0.23765 gram substance gave 0.5935 gram CO_2 and 0.0946 gram H_2O.

0.22005 gram substance gave 39.4 cc. N (742 mm. and 21°).

II. 0.1158 gram substance gave 20.4 cc. N (747.8 mm. and 15°.5).

	Calculated for $C_{24}H_{16}O_2N_6$.	Found. I.	II.
C	68.21	68.11	...
H	4.30	4.46	...
N	19.91	19.71	20.10

The product is hence resorcintrisazobenzene.

Diacetyl Derivative of Resorcintrisazobenzene Made from the Unsymmetrical Resorcindisazobenzene.—This product was made by the method already described and found to be absolutely identical with the two specimens of diacetylresorcintrisazobenzene already made. The yellow needles melting at 201° (uncor.) were analyzed:

0.15505 gram substance gave 0.3779 gram CO_2 and 0.0608 gram H_2O.

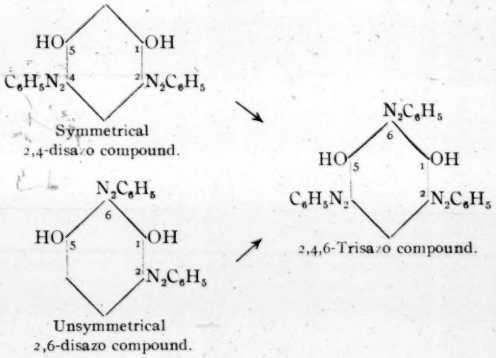
0.2095 gram substance gave 31.8 cc. N (739.5 mm. and 22°.5).

	Calculated for $C_{28}H_{22}O_4N_6$.	Found.
C	66.38	66.47
H	4.38	4.39
N	16.61	16.53

The product is hence diacetylresorcintrisazobenzene. It

crystallizes in the yellow and red modifications, which may be converted into each other by the methods already given.

Since it has been shown that the same resorcintrisazobenzene results from the combination of benzenediazonium chloride with the symmetrical and the unsymmetrical resorcindisazobenzenes, it follows that the azo groups must occupy the positions 2, 4 and 6. This is shown in the following scheme:



The So-called β-Resorcindisazobenzene of Wallach and Fischer.

The study of Wallach's so-called β-resorcindisazobenzene was next taken up. This compound was prepared by Wallach by combining one molecule of benzenediazonium chloride with resorcinazobenzene dissolved in four molecules of caustic potash. Two disazo compounds are formed here according to Wallach, one soluble and the other insoluble in aqueous alkalies. The first Wallach designates as the α- and the second as the β-resorcindisazobenzene. The α product yields a diacetyl derivative melting at 183° and is therefore the symmetrical 2,4-disazo compound, but the β product gives no well-crystallized acetyl derivative and its melting point is very difficult to determine accurately on account of its dark color. Important criteria for the absolute purity of the

β compound are therefore lacking. Wallach gives the melting point at 220° and states that it was earlier[1] given at "about 225°." He also states that the β compound dissolves in concentrated sulphuric acid with a pure indigo-blue color and in an alcoholic solution of caustic potash with a brownish-red color. The results of two determinations of carbon and hydrogen and one of nitrogen are given and these agree fairly well with the percentages of carbon, hydrogen and nitrogen calculated for the disazo formula, $(C_6H_5N_2)_2C_6H_2(OH)_2$, though the percentage of nitrogen found is nearly intermediate between that required for the disazo and the trisazo compounds.

In repeating the work of Wallach and Fischer, we first made resorcinazobenzene according to the directions of Kostanecki.[2] This was then converted into the so-called β-resorcindisazobenzene according to the directions of Wallach and Fischer, using the materials in the following proportions:

Resorcinazobenzene (1 mol.), 21.4 grams; caustic potash (4 mols.), 22.4 grams; aniline (1 mol.), 9.3 grams; sodium nitrite (1 mol.), 6.9 grams; hydrochloric acid (3 mols.), 10.9 grams.

On running the solution of the diazonium salt into the alkaline solution of the monazo compound, a dark brown precipitate slowly separated. The mixture was stirred for twenty-four hours and allowed to warm up to room temperature gradually. The finely divided precipitate was filtered off, suspended in dilute hydrochloric acid, washed with water, filtered and dried.

This crude product was crystallized from a mixture of chloroform and alcohol. Brownish microscopic needles were thus obtained, which corresponded to Wallach's description, as they melted at 221° (uncor.), were insoluble in aqueous alkalies, dissolved in concentrated sulphuric acid with a blue color, and formed a brownish-red solution in alcoholic caustic potash. When repeatedly crystallized from benzene and then from chloroform the melting point of the product rose to 228°.5 (uncor.). Several attempts were made to con-

[1] Ber. d. chem. Ges., **15**, 22.
[2] *Ibid.*, **21**, 3119.

vert this substance into an acetyl derivative, but without success. Nothing but tarry products were obtained. This is again in accord with Wallach's statements.

From the fact that this product was insoluble in aqueous alkalies, soluble in concentrated sulphuric acid with a blue color and in alkaline caustic potash with a brownish-red color, and from the method of preparation it was suspected that it was a trisazo compound. The product having the highest melting point, 228°.5, was then analyzed:

I. 0.0621 gram substance gave 11.25 cc N (733 mm. and 21°.5).

II. 0.10325 gram substance gave 19.25 cc. N (730 mm. and 25°).

	Calculated for:		Found.	
	Resorcin-disazobenzene.	Resorcin-trisazobenzene.	I.	II.
N	17.62	19.91	19.66	19.78

These analyses show that the product is resorcin*tris*azobenzene and not the *dis*azobenzene, as Wallach states. It differs, however, from the trisazo compound in its melting point and it was first thought that it might be a stereoisomer of this substance. Several attempts were therefore made to convert it into the trisazo compound melting at 254° by heating it with such high boiling solvents as xylene, nitrobenzene, etc., but no change took place. We then attempted to convert the trisazo compound melting at 254° into Wallach's β compound by dissolving it in alcoholic caustic potash, diluting with water and precipitating the compound with carbon dioxide. The product was dried in the air and recrystallized from chloroform. It melted at 254°, showing that it was unchanged by this treatment. Suspecting that the so-called β product was contaminated with a small amount of the symmetrical resorcindisazobenzene, which is soluble in aqueous solutions of the caustic alkalies, we made up a new lot of the β compound according to Wallach's directions and subjected the crude product to the following treatment: The material was suspended in two liters of a ten per cent. solution of caustic soda and the mixture treated with steam until it was near the boiling point and then filtered. The residue re-

maining on the filter was subjected to this treatment five or six times, with fresh sodium hydroxide solution each time, until it imparted but little color to the alkali solution. It was then suspended in dilute hydrochloric acid, washed with water, filtered and dried. The alkaline filtrates, when acidified, gave a voluminous precipitate of the symmetrical resorcindisazobenzene melting at 217° (uncor.). The material insoluble in dilute caustic soda solution, when crystallized from a mixture of chloroform and alcohol and from benzene, gave at once a product melting at 254° and identical with the resorcintrisazobenzene already described. It was then converted into the diacetyl derivative by the method given above and this was found to exist in the two modifications, yellow needles melting at 201° (uncor.) and red pyramidal crystals melting at 203° (uncor.), which could be converted into each other at will.

From these results it is evident that Wallach's so-called β-resorcindisazobenzene is an impure form of the resorcin-2,4,6-trisazobenzene.

Resorcin-2,4,6-trisazo-p-*toluene.*

This substance was prepared by the method already detailed in the preparation of resorcintrisazobenzene, substituting 32.1 grams of pure *p*-toluidine (3 mols.) for the 27.9 grams of aniline. The reddish-brown precipitate was filtered off after two days, thoroughly washed with water, suspended in dilute hydrochloric acid, again washed with water, filtered and dried. When repeatedly crystallized from a mixture of chloroform and alcohol and then from benzene until the melting point was constant, the product came out in the form of small reddish-brown needles which melted sharply at 259° (uncor.).

This compound is soluble in chloroform, benzene and toluene, slightly so in ethyl acetate and acetic acid, while it is practically insoluble in alcohol. It dissolves in alcoholic caustic potash with a reddish-brown color and in concentrated sulphuric acid, forming a reddish-violet solution.

Analyses showed that the compound is the resorcintrisazo-*p*-toluene, $C_6H(OH)_2(N_2C_7H_7)_3$.

0.24275 gram substance gave 40.4 cc. N (24° and 737 mm).

0.29925 gram substance gave 0.7651 gram CO_2 and 0.1375 gram H_2O.

	Calculated for $C_6H(OH)_2(N_2C_7H_7)_3$.	Found.
C	69.79	69.73
H	5.21	5.15
N	18.11	17.91

Diacetyl Derivative of Resorcin-2,4,6-trisazo-p-*toluene.*—This compound, made from the above product in the usual manner, crystallized from ethyl acetate and alcohol in yellow needles melting at 218° (uncor.). Analyses showed that it is the diacetyl derivative:

0.1885 gram substance gave 27.1 cc. N (20° and 724 mm.).

0.19095 gram substance gave 0.4747 gram CO_2 and 0.0865 gram H_2O.

	Calculated for $C_6H(OCOCH_3)_2(N_2C_7H_7)_3$.	Found.
C	67.85	67.80
H	5.15	5.08
N	15.33	15.51

In its solubility and physical properties this substance resembles the diacetylresorcintrisazobenzene very closely. It may also be obtained in two modifications, yellow needles and red prismatic crystals, which may be converted into each other by the methods given under diacetylresorcintrisazobenzene. The conversion of the yellow needles into the red crystals does not seem to take place so readily, however, as the ethereal solution must be boiled for some time before the transformation is complete.

Symmetrical Resorcindisazo-p-*toluene.*

Resorcindisazo-*p*-toluene was made by Wallach and Fischer[1] by combining resorcinazo-*p*-toluene with the diazonium salt obtained from *p*-toluidine in caustic potash solution. They obtained an α and a β compound, the latter in very considerable quantity. The α product, which is soluble in caustic alkalies,

[1] Ber. d. chem. Ges., **15**, 2824.

crystallizes in yellow felted needles, difficultly soluble in alcohol and cold chloroform, easily soluble in boiling chloroform, and melting at 255°–256°. Their β compound, insoluble in caustic alkalies, forms microscopic blackish-brown crystals, which, previous to crystallization from hot chloroform, dissolve in concentrated sulphuric acid with a red color and afterwards with a blue coloration. Melting point, 202°–203°. Analyses of both products are given and the percentages of carbon, hydrogen and nitrogen found, agree well with those required for the formula $(C_7H_7N_2)_2C_6H_2(OH)_2$. We made the symmetrical product by combining two molecules of *p*-toluenediazonium chloride and one of resorcin in sodium hydroxide solution, using the materials in the following proportions:

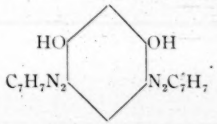
Resorcin (1 mol.), 11.0 grams; *p*-toluidine (2 mols.), 21.4 grams; sodium nitrite (2 mols.), 13.8 grams; hydrochloric acid (5 mols.), 18.25 grams; sodium hydroxide (4 mols.), 16.0 grams. The method given under the symmetrical resorcindisazobenzene was followed. The solution turned dark immediately on the addition of the diazonium salt and a dark brown precipitate formed. The mixture was stirred for two days without further addition of ice and then the dark brown precipitate, which was identical with Wallach's so-called β-resorcindisazo-*p*-toluene, was filtered off and laid aside for further study. On acidifying the filtrate a light brown precipitate was obtained, which was washed with water and dried. This was crystallized from chloroform and alcohol and gave reddish-brown needles melting at 254° (uncor.). It is soluble in chloroform, benzene, toluene, acetic acid, ethyl acetate, but only slightly soluble in alcohol and acetone. It dissolves in aqueous caustic alkalies with a reddish color and in concentrated sulphuric acid with a rose color. This compound is resorcindisazo-*p*-toluene, as shown by the following analyses:

0.1193 gram substance gave 18 cc. N (24° and 735.5 mm.).

0.19775 gram substance gave 0.50095 gram CO_2 and 0.09445 gram H_2O.

	Calculated for $C_6H_2(OH)_2(N_2C_7H_7)_2$.	Found.
C	69.33	69.09
H	5.24	5.35
N	16.19	16.20

It is identical with Wallach's α compound and from the method of formation it must have the symmetrical structure,



*Diacetyl Derivative of Symmetrical Resorcindisazo-*p*-toluene.*—This compound, prepared in the usual way, crystallized from a mixture of ethyl acetate and alcohol in light lemon-yellow needles, which melted at 198°.5 (uncor.) and gave the following result on analysis:

0.0797 gram substance gave 9.9 cc. N (22° and 722 mm).

	Calculated for $C_6H_2(OCOCH_3)_2(N_2C_7H_7)_2$.	Found.
N	13.03	13.23

Wallach's so-called β-resorcindisazo-*p*-toluene, which was obtained in the preparation of the symmetrical resorcindisazo-*p*-toluene, was next studied. Profiting by our experience in the investigation of the so-called β-resorcindisazobenzene of Wallach,[1] we placed the β-resorcindisazo-*p*-toluene in a large glass cylinder with two liters of a ten per cent. solution of caustic soda and passed steam into the mixture until it was near the boiling point. The hot solution was filtered and the process repeated until the residue imparted only a faint color to the alkali. It was then suspended in dilute hydrochloric acid, washed with water, filtered off and dried. On acidifying the filtrates from the above extractions the symmetrical resorcindisazo-*p*-toluene, melting at 254° (uncor.), was obtained.

Crystallization from chloroform and alcohol of the dried residue insoluble in the alkaline solution gave at once a product melting at 259° (uncor.), crystallizing in reddish-brown needles and corresponding in all other properties with the resorcintrisazo-*p*-toluene already described.[2] It gave a

[1] See page 23.
[2] See page 26.

diacetyl derivative crystallizing from ethyl acetate in yellow needles, melting at 218° and identical in all other properties with the diacetylresorcintrisazo-*p*-toluene already described. An analysis also proved this identity.

0.14845 gram substance gave 21.5 cc. N (25° and 729 mm.).

	Calculated for $C_6H(OCOCH_3)_2(N_2C_7H_7)_3$.	Found.
N	15.33	15.33

It seems highly probable from these results that Wallach's so-called *β*-resorcindisazo-*p*-toluene is in reality an impure resorcintrisazo-*p*-toluene from which he had not completely removed all of the disazo compound by his method of purification. The fact that this compound dissolves in concentrated sulphuric acid with a red color and, after purification by crystallization from hot chloroform, with a blue color indicates the same thing, since we have shown that the disazo product dissolves in sulphuric acid with a red color while the trisazo compound forms a reddish-violet solution in the same solvent.

*Unsymmetrical Resorcindisazo-*p*-toluene.*

As this compound had not been made we prepared it, using the materials in the following proportions:

Resorcin (1 mol.), 11 grams; *p*-toluidine (2 mols.), 21.4 grams; sodium nitrite (2 mols.), 13.8 grams; hydrochloric acid (5 mols.), 18.25 grams; sodium acetate (4 mols), 32.8 grams.

The *p*-toluidine was diazotized in the usual way and the resorcin added, the total amount of solvent being the same as in the preparation of the symmetrical resorcindisazo-*p*-toluene. The mixture was then poured slowly and with constant stirring into the sodium acetate dissolved in two liters of ice water. At first the combination takes place slowly and the reaction must be allowed to proceed at least two days. At the end of this time a beautiful salmon-colored precipitate had formed and this was washed thoroughly with water, filtered off and dried. When recrystallized from chloroform and alcohol it gave reddish-colored needles, melting at 230°.5 (uncor.).

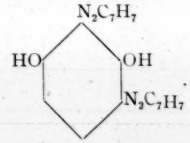
The compound is soluble in most of the organic solvents, but only slightly soluble in the aqueous caustic alkalies. On analysis it gave the following results:

0.17685 gram substance gave 26.2 cc. N (23° and 740.5 mm.).

0.1418 gram substance gave 0.3613 gram CO_2 and 0.0671 gram H_2O.

	Calculated for $C_6H_2(OH)_2(N_2C_7H_7)_2$.	Found.
C	69.33	69.49
H	5.24	5.30
N	16.19	16.12

The product is therefore resorcindisazo-*p*-toluene and from its method of formation it must have the unsymmetrical structure:



Diacetyl Derivative of the Unsymmetrical Resorcindisazo-p-toluene.

This substance was made from the above compound in the usual way. Crystallized from ethyl alcohol and ethyl acetate it gave orange-yellow needles melting at 150° (uncor.). Analyses show that it is a diacetyl derivative:

0.1079 gram substance gave 12.9 cc. N (19° and 733 mm.).

0.13135 gram substance gave 0.3214 gram CO_2 and 0.0614 gram H_2O.

	Calculated for $C_6H_2(OCOCH_3)_2(N_2C_7H_7)_2$.	Found.
C	66.94	66.74
H	5.15	5.23
N	13.03	13.14

Resorcin-2,4,6-trisazo-o-toluene.

In the preparation of this substance the same proportions of materials and the same method were used as in the case of

the para compound,[1] ortho- being simply substituted for the paratoluidine. After two days the heavy brown precipitate was filtered off, suspended in dilute hydrochloric acid, washed with water, filtered and dried. Crystallization from chloroform and from benzene gave prismatic, reddish-brown crystals which melted at 226° (uncor.). The compound is soluble in chloroform, benzene, toluene, xylene and aniline, very slightly soluble in alcohol. In alcoholic caustic alkali it dissolves with a reddish-brown color and in concentrated sulphuric acid with a reddish-violet color.

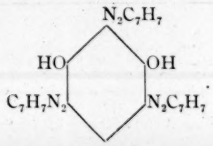
Analyses gave the following results:

0.16385 gram substance gave 27.3 cc. N (24°.5 and 742 mm.).

0.18225 gram substance gave 0.4663 gram CO_2 and 0.0859 gram H_2O.

	Calculated for $C_6H(OH)_2(N_2C_7H_7)_3$.	Found.
C	69.79	69.77
H	5.21	5.28
N	18.11	18.03

The compound is therefore resorcintrisazo-*o*-toluene and it is quite likely that the azo groups occupy the positions 2, 4 and 6 in the molecule:



Professor Gill reports as follows regarding the crystals: "The extremely minute lens-shaped crystals have very strong pleochroism, absorption across the length of the crystals being complete, while that lengthwise is a fairly light reddish-yellow. No definite idea of the crystal system could be formed, except that they are not regular."

Diacetyl Derivative of Resorcin-2,4,6-trisazo-o-toluene.—This substance crystallized from ethyl acetate and alcohol in red-

[1] See page 26.

dish-brown needles melting at 176° (uncor.). It is a diacetyl derivative, as shown by the following analyses:

0.0744 gram substance gave 10.4 cc. N (22° and 742 mm.).

0.11395 gram substance gave 0.2839 gram CO_2 and 0.0521 gram H_2O.

	Calculated for $C_6H(OCOCH_3)_2(N_2C_7H_7)_3$.	Found.
C	67.85	67.95
H	5.15	5.13
N	15.33	15.32

The crystals were examined by Professor Gill, who reports as follows: "The thinner needles show light yellow color, the thicker ones reddish-brown. Pleochroism is weak. The extinction angle varies from 0° to 15°, depending on the position of the needles. Those with high extinction angles show so strong dispersion that the angle cannot be accurately determined. They are certainly monoclinic or triclinic, probably the former."

Symmetrical Resorcindisazo-o-toluene.

Wallach and Fisher made this compound but they give no analyses of the product. We made it, using the materials in the following proportions:

Resorcin (1 mol.), 11 grams; *o*-toluidine (2 mols.), 21.4 grams; sodium nitrite (2 mols.), 13.8 grams; hydrochloric acid (5 mols.), 18.25 grams; sodium hydroxide (4 mols.), 16.00 grams. The method given under the symmetrical resorcindisazo-*p*-toluene was followed. At the end of thirty-six hours the dark brown precipitate, which is identical with Wallach's so-called *β*-resorcindisazo-*o*-toluene, was filtered off and put aside. The filtrate, when acidified, gave a light red precipitate, which was washed with water, dried and crystallized from chloroform and alcohol. Brown needles and dumbbell-shaped aggregates which melted at 197° (uncor.) were obtained. Wallach[1] gives the melting point as 194°–195°. Analyses show that it is the disazo product:

0.0816 gram substance gave 12.3 cc. N (24° and 742 mm.).

[1] Ber. d. chem. Ges., **15**, 2825.

0.0847 gram substance gave 0.21495 gram CO_2 and 0.0404 gram H_2O.

	Calculated for $C_6H_2(OH)_2(N_2C_7H_7)_2$.	Found.
C	69.33	69.21
H	5.24	5.24
N	16.19	16.36

Diacetyl Derivative of Resorcindisazo-o-toluene.—This product crystallized from ethyl acetate and alcohol in yellow needles melting at 178° (uncor.), which gave the following results on analysis:

0.0969 gram substance gave 11.5 cc. N (23° and 745 mm.).

0.1390 gram substance gave 0.3412 gram CO_2 and 0.0681 gram H_2O.

	Calculated for $C_6H_2(OCOCH_3)_2(N_2C_7H_7)_2$.	Found.
C	66.94	66.94
H	5.15	5.49
N	13.03	12.99

Wallach's so-called *β*-resorcindisazo-*o*-toluene[1] was shown to be a mixture of disazo and trisazo compounds by extracting it several times with hot caustic soda solution by the method already given[2] and crystallizing the residue from chloroform and alcohol. The crystals thus obtained melted at 222° (uncor.) while the pure resorcintrisazo-*o*-toluene melts at 226° (uncor.). The amount of material was so small that further purification was not possible but it seems quite likely from this melting point and the work done on the other *β* compounds that this product is also a mixture of the disazo and trisazo compounds.

Unsymmetrical Resorcindisazo-o-toluene.

This compound was made in the same way as the para compound, simply substituting *o*-toluidine for the *p*-toluidine.[3] The mixture was allowed to react three days and then the salmon-red precipitate was filtered off, washed with water and dried. Crystallized from chloroform and alcohol it gave

[1] Ber. d. chem. Ges., **15**, 2825.

[2] See page 25.

[3] See page 30.

brilliant red needles melting at 212° (uncor.), soluble in chloroform, benzene, xylene and slightly in alcohol. They are soluble in alcoholic caustic alkalies with a red color and in concentrated sulphuric acid, forming a beautiful rose-colored solution. Analyses showed that it is the disazo product:

0.2363 gram substance gave 34.7 cc. N (745 mm. and 22°).

0.1683 gram substance gave 0.4279 gram CO_2 and 0.0799 gram H_2O.

	Calculated for $C_6H_2(OH)_2(N_2C_7H_7)_2$.	Found.
C	69.33	69.34
H	5.24	5.32
N	16.19	16.15

Professor Gill states: "The crystals are somewhat flattened needles, with strong pleochroism and very high double refraction. The extinction angle reaches 30° as a maximum and is nearly zero as a minimum. The light transmitted vibrating in the direction of elongation is light yellowish in color, while that vibrating transversely is of a reddish hue. The crystals are either triclinic or monoclinic."

Diacetyl Derivative of Unsymmetrical Resorcindisazo-o-toluene.

This compound was prepared in the usual way and after crystallization f om ethyl acetate and alcohol was obtained as orange-yellow needles melting at 130° (uncor.). Analyses resulted as follows:

0.14085 gram substance gave 17 cc. N (21° and 732 mm.).

0.1214 gram substance gave 0.29865 gram CO_2 and 0.0548 gram H_2O.

	Calculated for $C_6H_2(OCOCH_3)_2(N_2C_7H_7)_2$.	Found.
C	66.94	66.94
H	5.15	5.06
N	13.03	13.11

Professor Gill finds that "there are two kinds of crystals, one kind being apparently like those of the resorcintrisazo-*o*-toluene. The others are nonpleochroic or very slightly pleochroic, reddish-yellow needles with parallel extinction."

Resorcin-2,4,6-trisazo-α-naphthalene.

The following proportions of materials were used in the preparation of this substance:

Resorcin (1 mol.), 11 grams; α-naphthylamine (3 mols.), 42.9 grams; sodium nitrite (3 mols.), 20.7 grams; hydrochloric acid (7 mols.), 25.5 grams; sodium hydroxide (5 mols.), 20 grams.

Owing to the fact that naphthalenediazonium chloride combines immediately with any unchanged α-naphthylamine present, special precautions had to be taken in diazotizing the α-naphthylamine. Very dilute solutions must be employed and the process carried out very rapidly. The 42.9 grams of α-naphthylamine were suspended in four liters of water, the total amount of hydrochloric acid added and the mixture warmed until solution was effected. This solution was then cooled with ice to 0° and poured rapidly and with vigorous stirring into the sodium nitrite dissolved in one liter of ice water. If the process is carried out rapidly enough a perfectly clear solution of the diazonium salt results. To this, the resorcin, dissolved in 100 cc. of ice water, was added, the mixture stirred for 10 minutes and then poured slowly and with constant stirring into the alkali dissolved in two liters of ice water. The mixture was stirred for two days and gradually allowed to warm up to the temperature of the room. The heavy black precipitate was filtered off, suspended in dilute hydrochloric acid, washed thoroughly with water, filtered and dried. The yield of the trisazo compound was practically quantitative.

The dry product was then put into a large Soxhlet extractor and thoroughly extracted with absolute alcohol to remove substances soluble in this solvent. The residue left in the extractor, when crystallized from chloroform, gave small prisms having a cantharides-green luster. From benzene it comes out in clusters of prismatic needles melting at 253°. These were submitted to Professor Gill, who reports as follows: "Crystals absorb too strongly to transmit light even through the thinnest edges. On crushing, the very smallest fragments (under 0.001 mm.) show purplish and have an ex-

tinction, thereby proving extremely high double refraction. The thin film made by crushing with the nail is clear purplish-red in transmitted light, not doubly refracting."

The compound is soluble in chloroform, benzene, toluene, xylene and aniline, very slightly soluble in ethyl acetate, acetone and glacial acetic acid, while it is insoluble in ether and alcohol. It dissolves in concentrated sulphuric acid with a reddish-violet color.

Analyses gave the following results:

I. 0.1268 gram substance gave 0.3511 gram CO_2 and 0.0507 gram H_2O.

II. 0.1751 gram substance gave 0.4852 gram CO_2 and 0.0681 gram H_2O.

0.0966 gram substance gave 13.15 cc. N (22° and 730 mm.).

	Calculated for $C_6H(OH)_2(N_2C_{10}H_7)_3$.	Found. I.	Found. II.
C	75.49	75.51	75.57
H	4.23	4.48	4.36
N	14.69	...	14.67

The compound is therefore resorcintrisazo-α-naphthalene.

Diacetyl Derivative of Resorcin-2,4,6-trisazo-α-naphthalene.—On account of the slight solubility of the resorcintrisazo-α-naphthalene it was necessary to use a large amount of acetic anhydride in converting it into its diacetyl derivative. After boiling for several hours with a large excess of the anhydride, the material unacted on was filtered off and again boiled with fresh anhydride until it was all dissolved. The anhydride was then distilled off almost entirely, the residue poured into cold water, and the product crystallized from ethyl acetate and alcohol. Yellow prisms and cigar-shaped needles resulted, which melted sharply at 228° (uncor.). Analyses:

0.11665 gram substance gave 0.3121 gram CO_2 and 0.04565 gram H_2O.

0.05965 gram substance gave 6.75 cc. N (19° and 741 mm.).

	Calculated for $C_6H(OCOCH_3)_2(N_2C_{10}H_7)_3$.	Found.
C	73.14	72.98
H	4.30	4.39
N	12.81	12.57

On boiling with ether these yellow needles go over into red tabular crystals, the transformation being similar to that observed in the case of the diacetyl derivative of resorcin-2,4,6-trisazobenzene.

The two forms are thus described by Professor Gill: "The very small capillary yellow crystals show no appreciable pleochroism and give extinction angles varying from 0° to several degrees. It behaves like the following modification, with which it may well be isomorphous."

"The extremely minute pleochroic blood-red to yellowish-red crystals are of stout tabular to columnar habitus and show parallel extinction in all positions. They are probably orthorhombic."

Symmetrical Resorcindisazo-α-naphthalene.

Many attempts were made to obtain this compound, but without success. When an alkaline solution of resorcin was treated with two molecules of α-naphthalenediazonium chloride the resorcin*trisazo*-α-naphthalene resulted in every case and this compound was also obtained when resorcinazo-α-naphthalene in alkaline solution was treated with one molecule of the naphthalenediazonium salt.

Unsymmetrical Resorcindisazo-α-naphthalene.

The following proportions of materials were used in preparing this compound:

Resorcin (1 mol.), 2.75 grams; α-naphthylamine (2 mols.), 7.15 grams; sodium nitrite (2 mols.), 3.45 grams; hydrochloric acid (5 mols.), 4.55 grams; sodium acetate (4 mols.), 8.20 grams.

The solution of the diazonium salt, prepared according to the directions already given, was added to the resorcin dissolved in 50 cc. of ice water. This mixture was then poured slowly and with constant stirring nto the sodium acetate dissolved in one liter of ice water. The solution turns reddish at first, then brown, and finally a brown precipitate settles out. After stirring the mixture for two days the precipitate was filtered off, washed with water and dried. Repeated

crystallization from a mixture of choroform and alcohol and from benzene until the melting point was constant gave very fine light brown needles, melting at 242° (uncor.), which dissolve in aqueous caustic soda with a reddish color. The following analyses show that it is the disazo compound:

0.11475 gram substance gave 0.31415 gram CO_2 and 0.0484 gram H_2O.

0.08435 gram substance gave 10.3 cc. N (19° and 726.5 mm).

	Calculated for $C_6H_2(OH)_2(N_2C_{10}H_7)_2$.	Found
C	74.61	74.66
H	4.34	4.72
N	13.40	13.29

Diacetyl Derivative of Unsymmetrical Resorcindisazo-α-naphthalene.—This product, made in the usual way from the disazo compound and crystallized from chloroform and alcohol, forms fine yellow needles melting at 142° (uncor.). Analyses made by Mr. J. K. Plummer gave the following results:

I. 0.1332 gram substance gave 14.3 cc. N at 26° C. Barometer 748 mm. at 24°.2 C.

II. 0.1315 gram substance gave 13.95 cc. N at 24° C. Barometer 747 mm. at 23° C.

	Calculated for $C_6H(OCOCH_3)_2(N_2C_{10}H_7)_2$.	Found. I.	II.
N	11.16	11.61	11.59

*Bisazobenzene-*p*-diazoaminoazobenzene,*

$$(C_6H_5N_2C_6H_4N_2)_2NC_6H_4N_2C_6H_5.$$

This compound was obtained in an attempt to prepare a trisazo product by diazotizing *p*-aminoazobenzene and combining it with an alkaline solution of resorcin in the proportions of three molecules of the former to one of the latter. It is formed very readily on adding a cooled alcoholic solution of aminoazobenzene (3 mols.) and acetic acid (9 mols.) to a cold solution of sodium nitrite (2 mols.). Hence the compound is a condensation product of diazotized aminoazobenzene with aminoazobenzene. It crystallizes from 95 per cent. alcohol in yellow leaflets melting at 184° (uncor.).

It is insoluble in aqueous caustic alkalies, dissolves in concentrated sulphuric acid with a red color and in alcoholic caustic alkalies with a reddish-violet color. Analyses gave the following results:

I. 0.1017 gram substance gave 0.2627 gram CO_2 and 0.0419 gram H_2O.

II. 0.0717 gram substance gave 0.1850 gram CO_2 and 0.0301 gram H_2O.

0.0493 gram substance gave 11.15 cc. N (22° and 741 mm.).

	Calculated for $(C_6H_5N_2C_6H_4N_2)_2NC_6H_4N_2C_6H_5$.	Found. I.	Found. II.
C	70.43	70.44	70.36
H	4.44	4.61	4.71
N	25.13	...	24.74

The product is therefore a bisdiazoamino compound formed according to the following equation:

$$2C_6H_5N_2C_6H_4N_2OH + H_2NC_6H_4N_2C_6H_5 = (C_6H_5N_2C_6H_4N_2)_2NC_6H_4N_2C_6H_5 + 2H_2O.$$

Professor Gill thus describes the crystals: "The substance occurs in masses of overlapping plates which show distinct pleochroism—from brownish-yellow to pale yellow—a biaxial interference figure, medium double refraction and inclined extinction. The crystals are probably triclinic in form."

The more important facts brought out in this investigation may be briefly summarized as follows:

1. Resorcin-2,4,6-trisazobenzene has been prepared by the action of three molecules of benzenediazonium chloride on resorcin in caustic alkaline solution, as well as by the action of one molecule of the diazonium salt on the symmetrical and on the unsymmetrical resorcindisazobenzenes in cautic alkaline solution. This shows the position of the azo groups in the molecule to be 2, 4 and 6.

2. Wallach's so-called β-resorcindisazobenzene has been made and shown to be an impure product, containing resorcintrisazobenzene mixed with some symmetrical resorcindisazo-

benzene. It is probable that Wallach's β-resorcindisazo-*o*- and *p*-toluenes are also impure trisazo compounds.

3. The diacetyl derivative of resorcin-2,4,6-trisazobenzene has been made and shown to exist in two modifications, one crystallizing from absolute alcohol in yellow needles and the other from ether in red pyramidal crystals, the latter being the more stable form.

4. Resorcin-2,4,6-trisazo-*o*- and *p*-toluenes and their diacetyl derivatives, and the unsymmetrical resorcindisazo-*o*- and *p*-toluenes and their diacetyl derivatives have been made.

5. Resorcin-2,4,6-trisazo-α-naphthalene has been prepared and converted into its diacetyl derivative, which also exists in two modifications, one crystallizing from alcohol in yellow needles, the other in red pyramidal crystals. The unsymmetrical resorcindisazo-α-naphthalene and its diacetyl derivative have also been made.

6. Bisazobenzene-*p*-diazoaminoazobenzene,

$$(C_6H_5N_2C_6H_4N_2)_2NC_6H_4N_2C_6H_5,$$

has been made and described.

CORNELL UNIVERSITY,
ITHACA, N. Y.,
March, 1910.

A GENERAL REACTION FOR THE CONVERSION OF SATURATED FATTY ACIDS ($R.CH_2.CH_2.COOH$) INTO KETONES ($R.CO.CH_3$).

BY H. D. DAKIN.

It is a well established fact that in the diabetic organism butyric acid is oxidized to β-hydroxybutyric acid, and the latter substance is converted by the action of enzymes[1] present in the liver into acetacetic acid, which in part loses carbon dioxide with formation of acetone:

$$CH_3.CH_2.CH_2.COOH \longrightarrow CH_3.CH(OH).CH_2.COOH \longrightarrow CH_3.CO.CH_2.COOH \longrightarrow CH_3.CO.CH_3 + CO_2.$$

[1] Cp. Wakeman and Dakin: J. Biol. Chem., **6**, 373.

There is good reason to believe that an essentially similar series of reactions takes place in the normal animal, but under physiological conditions the β-hydroxybutyric acid and acetacetic acid are quantitatively decomposed so that they are not found in normal urine.

From results recently obtained by the writer it appears probable that acetacetic acid is the primary product of oxidation of butyric acid in the animal body and that the acetacetic acid thus formed undergoes asymmetric reduction in the liver to *l*-β-hydroxybutyric acid.

The type of oxidation represented by the conversion of butyric acid into β-hydroxybutyric and acetacetic acids, regarded from a purely chemical point of view, is a very remarkable one, and some writers have refused to accept excellent biochemical evidence of its occurrence on the ground that no purely chemical analogy for such a reaction was known.

Three years ago the writer[1] showed that by a suitable choice of oxidizing agent it was possible to oxidize butyric acid outside the body in a way that bore a close resemblance to its mode of oxidation in the living organism. It was found that when neutralized with ammonia and digested at a low temperature (37°) with hydrogen peroxide it was converted in part into acetacetic acid and acetone. If the substances were gently boiled together, the yield of acetone was quite large. Under favorable conditions as much as fifty per cent. of the theoretical amount of acetone, calculated upon the amount of butyric acid actually oxidized, was obtained. Among other products of oxidation the following were detected: propionic aldehyde, acetic aldehyde, acetic and formic acids and carbon dioxide. No β-hydroxybutyric acid could be detected.

On further investigation it was found that the same type of reaction could be demonstrated to occur in the case of some higher fatty acids.[2] The object of the following paper is to record the results of further experiments which show that the reaction is a general one. In every case it has been

[1] J. Biol. Chem., **4**, 77.
[2] *Ibid.*, **4**, 221.

possible to demonstrate the formation of a ketone by boiling a solution of the ammonium salt of a higher fatty acid with hydrogen peroxide and it is natural to infer that the ketone is derived from a β-ketonic acid, as is undoubtedly the case when butyric acid is oxidized with formation of acetone:

$$R.CH_2.CH_2.COOH \longrightarrow R.CO.CH_2.COOH \longrightarrow R.CO.CH_3 + CO_2.$$

It was considered possible that fatty acid superoxides of the type described by Brodie[1] might be intermediary products in the process of oxidation. This appears unlikely, however, since butyryl superoxide, prepared by the action of barium peroxide upon an ethereal solution of butyric anhydride, failed to yield significant amounts of acetone when boiled with water or dilute alkali.

Propionic acid, when oxidized under the same conditions as those adopted in the case of butyric acid, yields acetaldehyde. It is possible, though perhaps unlikely, that this is also a case of oxidation of an acid in the β position, with formation of the half aldehyde of malonic acid as an intermediate step, followed by subsequent decomposition into acetaldehyde and carbon dioxide:

$$CH_3.CH_2.COOH \longrightarrow HOC.CH_2.COOH \longrightarrow HOC.CH_3 + CO_2.$$

Acetic acid, on the other hand, yields glyoxylic acid and formaldehyde, together with much formic acid.[2]

Similar results were also obtained on oxidizing the phenyl derivatives of fatty acids; phenylacetic acid yields benzaldehyde, while phenylpropionic acid and phenylbutyric acid yield acetophenone and benzylmethylketone(?), respectively.

The results are collected in the following table, in which no cognizance is taken of products of oxidation other than ketones and aldehydes. In its present form the reaction under consideration is of no value for preparative purposes, since the yields are usually so small—averaging not more than 5–10 per cent.:

[1] J. Chem Soc., **1863,** 317.
[2] Cp. Hopkins: P. Roy. Soc., **67,** 21.

Acid oxidized.	Product.
Acetic acid.	Glyoxylic acid : formaldehyde (Hopkins).
Propionic acid.	Acetaldehyde.
n-Butyric acid.	Acetone
Isobutyric acid.	Acetone.
n-Valeric acid.	Ethylmethyl ketone.
Isovaleric acid.	Acetone.
n-Caproic acid.	Propylmethyl ketone.
Caprylic acid.	Amylmethyl ketone.
Nonylic acid.	Hexylmethyl ketone.
Capric acid.	Heptylmethyl ketone.
Lauric acid.	Nonylmethyl ketone.
Myristic acid.	Undecylmethyl ketone.
Palmitic acid.	Tridecylmethyl ketone.
Stearic acid.	Quindecylmethyl ketone.
Phenylacetic acid.	Benzaldehyde.
Phenylpropionic acid.	Acetophenone.
Phenylbutyric acid.	Benzylmethyl ketone(?)

EXPERIMENTAL.

The methods employed in the experiments to be recorded were very simple and require but little description.[1] The oxidations in all cases were carried out by heating, to a point just short of active boiling, a mixture of the fatty acid, neutralized with a slight excess of ammonia or caustic soda and a large excess of dilute (3 per cent.) hydrogen peroxide. The materials are contained in large flasks connected with a reflux condenser, since foaming is apt to be very troublesome, particularly in the case of the higher fatty acids. The exact amount of hydrogen peroxide is of no great consequence, since under the most favorable conditions only a part of the fatty acid undergoes oxidation. Using 2 molecules of peroxide and one molecule of fatty acid, the proportion of fatty acid oxidized is less than ten per cent. in the case of the acids higher than caproic acid, but more than ten per cent. in the case of the lower fatty acids.[2]

In the case of the fatty acids up to and including lauric acid, the liquid containing the products of oxidation was

[1] Cp. papers in J. Biol. Chem., already referred to.
[2] Cp. J. Biol. Chem., **4**, 229.

distilled. The distillate contains the ketone usually mixed with some aldehydes and also contains ammonia when that base was used for neutralizing the fatty acid prior to oxidation. The distillates from caprylic, nonylic, capric and lauric acids contain ketones which are very sparingly soluble in water and the oil drops are readily separated from the aqueous portion of the distillate and converted into a characteristic crystalline derivative. For purposes of identification, the *p*-nitrophenylhydrazones were found very useful.[1]

The distillate from the fatty acids lower than caprylic acid were treated as follows: A small quantity of Tollen's ammoniacal silver solution containing caustic soda was added and the mixtures allowed to stand for about an hour in order to oxidize any aldehyde present. They were next acidified strongly with phosphoric acid and redistilled. The ketones coming over in the first portion of the distillate were then identified by conversion into crystalline derivatives.

The ketones obtained from the oxidation of myristic, palmitic and stearic acids were isolated as follows: The alkaline mixture containing the products of oxidation was acidified with sulphuric acid and the precipitated fatty acids, ketone, etc., filtered off and washed. The precipitate was then dissolved in excess of alcoholic potash and evaporated to small bulk; the soapy residue was then dissolved in hot water and the solution extracted with ether. The ethereal solution, which is apt to contain traces of soap, is well washed with water and the ether distilled off. The residue is distilled from a small flask under reduced pressure. The distillate collected at about the temperature at which the ketone would be expected to distil is recrystallized from dilute alcohol and identified by melting point and by analysis:

A brief summary of the results upon which the identification of the products of oxidation is based is appended:

Propionic Acid.—The acetaldehyde was converted into the *p*-nitrophenylhydrazone, melting at 128°,[2] and was further identified by the usual reactions.

[1] Cp. J. Biol. Chem., **4**, 235.
[2] Hyde: Ber. d. chem. Ges., **32**, 1810.

Butyric Acid.—The acetone produced by the oxidation of butyric acid was identified by conversion into dibenzylidenacetone, melting at 111°.5–112°.5 on treatment with benzaldehyde and caustic soda, and also into the *p*-nitrophenylhydrazone, melting at 149°.[1] (Analysis: C = 56.2, H = 5.9; $C_9H_{11}O_2N_3$ requires C = 56.0, H = 5.7.)

Isobutyric Acid.—The methods of identification were the same as those employed in the case of *n*-butyric acid.

n-*Valeric Acid.*—The ethylmethyl ketone obtained on oxidation gave the *p*-nitrophenylhydrazone, melting at 128°, which crystallizes from alcohol in long yellow needles. (Analysis: C = 58.2, H = 6.5; $C_{10}H_{13}O_2N_3$ requires C = 57.9, H = 6.3.)

Isovaleric Acid.—The acetone was identified as in the case of butyric acid.

n-*Caproic Acid.*—Propylmethyl ketone was obtained on oxidation and converted into the *p*-nitrophenylhydrazone, which crystallizes from alcohol in long golden prismatic needles, melting at 117°. This substance has not been previously described and was therefore prepared for purposes of comparison from a specimen of pure propylmethyl ketone of other origin. The two substances were identical in every respect. (Analysis: N = 18.8 per cent.; $C_{11}H_{15}O_2N_3$ requires 19.0 per cent. N.)

Caprylic Acid.—The oily amylmethyl ketone from the oxidation of this acid was identified by conversion into the semicarbazone, melting at 122°–123°.[2]

Nonylic Acid.—The hexylmethyl ketone was identified by conversion into the *p*-nitrophenylhydrazone, which after repeated crystallization from alcohol was obtained in the form of aggregates of yellow prisms melting at 92°–93°. For purposes of comparison the same substance was prepared from hexylmethyl ketone of other origin.

Capric Acid.—Heptylmethyl ketone was identified by means of its semicarbazone, which, after recrystallization from alcohol, melted at 118°–119°. The substance was identical

[1] J. Biol. Chem., **4**, 77.
[2] Cp. J. Biol. Chem., **4**, 221.

with that previously prepared by Thoms and by Soden and Henle.

Lauric Acid.—The sparingly soluble volatile oily ketone was identified by conversion into the *p*-nitrophenylhydrazone and also the semicarbazone melting at 122°–122°.5. The nitrophenylhydrazone crystallizes from alcohol in yellow needles often arranged in rosette form, melting at 90°–91°. The product was identical with that obtained from methylnonyl ketone of other origin. (Analysis: C = 66.8, H = 8.8; $C_{17}H_{27}O_3N_3$ requires C = 66.9, H = 8.8.)

Myristic Acid.—The products of oxidation of myristic acid were treated with potash and then extracted with ether in the manner referred to on p. 45. On distilling the ether residue from a small flask a small quantity of undecylmethyl ketone was obtained from the fraction boiling between 245°–265°. It was crystallized from a little cold dilute alcohol and melted at 27°–28°, agreeing with Krafft's[1] observations. (Analysis: C = 78.6, H = 13.3; $C_{13}H_{26}O$ requires C = 78.8, H = 13.1.)

Palmitic Acid.—Tridecylmethyl ketone was obtained from the fraction boiling below 200° under 22 mm. pressure. It was recrystallized from alcohol and melted at 39°—the melting point given by Krafft.

Stearic Acid.—Quindecylmethyl ketone was obtained from the fraction boiling below 210° under 20 mm. pressure. It crystallized from alcohol in large glistening, irregularly formed plates, melting at 48°–49°. (Analysis: C = 79.9, H = 13.3; $C_{17}H_{34}O$ requires C = 80.3, H = 13.4.)

Phenylacetic Acid.—This acid was oxidized in the way that had already proved serviceable in the case of phenylpropionic acid.[2] Benzaldehyde was readily identified by conversion into the phenylhydrazone, melting at 156°. Small amounts of aromatic hydroxy acids were formed at the same time.

Phenylpropionic Acid.—A description of the oxidation of

[1] Ber. d. chem. Ges., **12**, 1667; **15**, 1724.
[2] J. Biol. Chem., **4**, 428.

this acid has already been published.[1] Acetophenone was readily obtained and identified by conversion into the *p*-nitrophenylhydrazone melting at 184°–185°. Aromatic hydroxy acids were also formed.

Phenylbutyric Acid.—The oxidation of phenylbutyric acid was carried out as in the case of phenylpropionic acid. It was easy to demonstrate the formation of a volatile ketone with the odor of benzylmethyl ketone, but with the small amount of acid (3.0 grams) available for oxidation it was not found possible to obtain a sufficient amount of the ketone, free from contaminating aldehydes formed simultaneously, to obtain the nitrophenylhydrazone in the pure state. The ketone reacted in the iodoform and nitroprusside tests in the same manner as pure benzylacetone.

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THE CATALYTIC RACEMIZATION OF OPTICALLY ACTIVE HYDANTOIN DERIVATIVES AND OF RELATED SUBSTANCES AS THE RESULT OF TAUTOMERIC CHANGE.

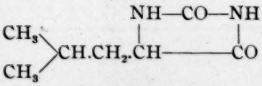
BY H. D. DAKIN.

The optically active α-amino acids of the general type $R.CH.NH_2.COOH$ are readily converted by the action of potassium cyanate into the salts of the corresponding uramido acids, $R.CH\langle^{NH.CO.NH_2}_{COOH}$, and then by the action of boiling dilute mineral acids are transformed into the corresponding hydantoins, $R.CH\langle^{NH—CO}_{CO—NH}$, through loss of a molecule of water. A study of a number of these derivatives of amino acids has recently been made since they appear to possess some biological significance. In the course of this investigation it was found convenient to ob-

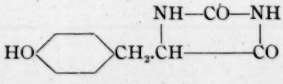
[1] J. Biol. Chem., **4**, 419.

serve the optical activity of both the uramido acids and the hydantoins in alkaline solutions, since most of them are sparingly soluble in water but readily form soluble salts. It was found that under these conditions the optical rotation of the uramido acids was constant, whereas the rotation of the hydantoin derivatives steadily diminished until after the lapse of many hours the solution was optically inactive. On acidifying the solution which had originally contained the optically active hydantoin, the inactive hydantoin was recovered in every case, showing that the change that the substance had undergone was simply that of racemization. The inactive products thus obtained were in several instances compared with the hydantoins obtained synthetically from optically inactive amino acids.

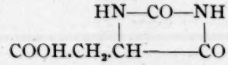
The following optically active hydantoins have in each case shown a rapid loss of optical activity when dissolved in normal caustic soda solution:



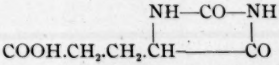
Isobutylhydantoin prepared from *l*-leucine.



p-Hydroxybenzylhydantoin prepared from *l*-tyrosine.



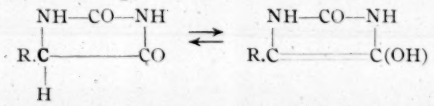
Hydantoinacetic acid prepared from *l*-aspartic acid.



Hydantoinpropionic acid prepared from *d*-glutamic acid.

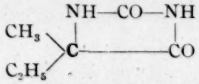
It was clearly of interest to try to elucidate the mechanism of this curious process of racemization. The fact that, in contrast with the optically active hydantoins, the active uramido acids show no trace of any such change in optical activity under like conditions indicated that the process of racemization was intimately connected with the presence of the CH—CO grouping. It was considered likely that the salts of the hydantoins might be derived from two tautomeric forms of hydantoin, only one of which contains an asym-

metric carbon atom. The two forms may be represented as follows:



Containing asymmetric carbon atom. No asymmetric carbon atom.

It is clear that such a type of tautomerism, if occurring in the hydantoin salts, would furnish a ready explanation of their racemization in the presence of alkali. Fortunately, it has been possible to make what appears to be a crucial test of this hypothesis. Owing to the kindness of Dr. Felix Ehrlich, a small quantity of *l*-methylethylaminoacetic acid (isovalin) was placed at my disposal and this was converted in the usual way, successively, into the corresponding uramido acid and hydantoin. The resulting methylethyl hydantoin was optically active but showed no sign of racemization in the presence of alkali. The reason of this is obviously to be sought in the absence of a labile hydrogen atom, without which the type of tautomeric change indicated



Methylethyl hydantoin.

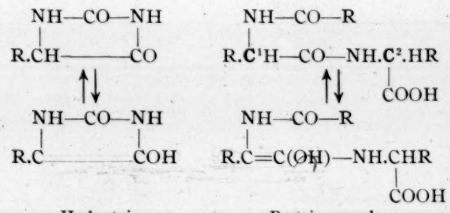
above cannot take place.

In the light of the above experiment, it can hardly be doubted that tautomeric change of the keto-enol type takes place in the salts of hydantoins containing the —CH—CO— grouping, and such an explanation adequately accounts for all the observed facts. I am unaware of the previous description of tautomerism of this type among the cyclic ureides.

The course of the racemization of the active hydantoins may be readily followed by means of the polarimeter. The reaction is apparently a monomolecular one, but the change has not yet been followed with great accuracy. The nature of the alkali exerts a profound influence upon the speed of

racemization. Thus, in an experiment in which hydantoin-acetic acid was dissolved in 0.25 N alkali so that 4 molecules of alkali were present to 1 molecule of hydantoin, 90 per cent. racemization was reached in 20 hours in the case of barium hydroxide, 33 hours with sodium hydroxide and 55 hours when ammonia was used. These differences may be due to the varying dissociation of the individual alkalies and salts. Provided sufficient time is allowed to elapse, complete racemization of 1 molecule of hydantoin may be effected by less than 1 molecule of alkali.

Since the molecular arrangement of the hydantoin ring bears a close resemblance to the groupings of amino acid radicals present in protein molecules, it was thought probable that proteins and their derivatives would also exhibit racemization phenomena when digested with dilute alkali. The groupings in the two cases may be compared as follows:



Hydantoin. Protein complex.

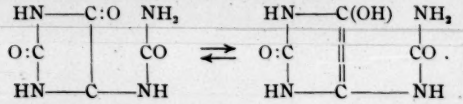
It was found that on dissolving egg albumin, gelatin, protamine, or Witte's peptone in normal caustic soda, a marked diminution in rotatory power was observed after the lapse of a few hours and it steadily continued for several days. Thus a solution of egg albumin in 0.5 N caustic soda[1] had an initial rotation of —1°.40 in a 200 mm. tube. After standing at room temperature for a week the value of α had fallen to —0°.82. Under similar conditions a solution of peptone in N sodium hydroxide[2] had an initial rotation of —9°.44, which fell to —2°.0 after five days. In no case did the op-

[1] The solution contained 0.169 per cent. nitrogen.
[2] The solution contained 1.18 per cent. nitrogen.

tical activity entirely disappear. This is in complete accord with what one would anticipate, since the hypothesis advanced would indicate that only those amino acid groupings which have undergone mutual condensation with elimination of water would be racemized. Free amino acid groupings, —CHR.NH—COOH, such as are undoubtedly present in protein molecules, would be unaffected, since here, as in the case of the uramido acids, keto-enol tautomerism cannot occur. Thus for the two asymmetric carbon atoms present in the protein complex (see formula above), racemization would occur only in relation to the asymmetric group marked (1), and not in the case of that marked (2).

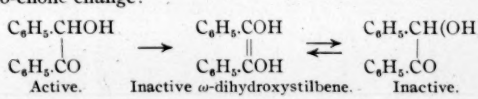
After my observations on the racemization of proteins had been made, I learned that Kossel and Weiss[1] had made similar experiments about a year previously. A careful study of the products of hydrolysis of "racemized proteins" would undoubtedly furnish valuable results, and such an investigation is, I believe, planned by Professor Kossel.

The conception of racemization due to keto-enol tautomeric change has recently been applied by Mendel and the writer to account for the optical inactivity of allantoin.[2] The customary formula for allantoin contains an asymmetric carbon atom, yet the substance, when isolated from natural sources, such as the urine of dogs fed with thymus, is constantly inactive and all attempts to resolve the inactive substance by chemical or biological methods have failed. Now allantoin may be regarded as the ureide of hydantoin and may be assumed to exhibit tautomerism of the same kind as is observed in the case of other hydantoin derivatives. The result of such tautomeric change would obviously lead to an optically inactive product since one of the two tautomeric forms contains no asymmetric carbon atom:



[1] Z. physiol. Chem., **50**, 492.
[2] J. Biol. Chem., **1**, 153.

In conclusion, reference may be made to an interesting paper by Wren,[1] in which he shows that the racemization of *l*-benzoin and its methyl ether is probably to be referred to keto-enolic change:



Active. Inactive ω-dihydroxystilbene. Inactive.

The racemization of *d*-β-methylhydrindone observed by Kipping,[2] and the conversion of *l*-menthone into *d*-menthone may also be due to tautomeric change of a similar kind.

EXPERIMENTAL.

d-α-*Uramidoisobutylacetic Acid.*—The laevorotatory leucine which served for the preparation of this acid was obtained by the hydrolysis of gelatin and was purified by conversion into the ethyl ester which was fractionated *in vacuo* and then hydrolyzed by boiling with water. The leucine was then repeatedly crystallized from water. It is unlikely, however, that the product was optically absolutely pure, since it is extremely difficult to obtain preparations of leucine entirely free from its isomers. The conversion into the uramido acid was readily effected by mixing leucine (5 grams) with potassium cyanate (5 grams) and adding 20 cc. of water. The mixture was then evaporated on the water bath almost to dryness. The residue was dissolved in a little hot water, filtered, and the crude uramido acid precipitated by the addition of hydrochloric acid. The yield of uramido acid amounts to about 70 per cent. of the theoretical amount. The substance was purified by repeated crystallization from boiling water and separates in the form of prismatic needles, melting at 205°–206°[3] with effervescence.

Analysis:

0.2130 gram substance gave 0.3705 gram CO_2 and 0.1590 gram H_2O.

[1] J. Chem. Soc., **95**, 1593.

[2] P. Chem. Soc., **18**, 34. J. Chem. Soc., **95**, 167.

[3] Lippich (Ber. d. chem. Ges., **41**, 2963) obtained this substance by the action of urea upon leucine in the presence of baryta. The melting point is given as 189°. It is possible that Lippich's substance was partly racemized.

	Calculated for $C_7H_{14}O_3N_2$.	Found.
C	48.28	47.91
H	8.04	8.29

The optical rotation was observed by dissolving the substance in normal caustic soda solution:

$c = 3.15$, $l = 2.0$, $\alpha = +1°.25$, hence $[\alpha]_D^{20} = +1°.9$.

No change in the rotation was observed after the solution had stood for more than 48 hours.

l-*Isobutylhydantoin.*—On boiling *d*-α-uramidoisobutylacetic acid with ten per cent. hydrochloric acid (10 parts) for half an hour the substance was readily converted into the corresponding hydantoin, which crystallized out on cooling in transparent prismatic needles, melting at 212°. The substance is readily purified by recrystallization from boiling water.

Analysis:

0.1430 gram substance gave 0.2802 gram CO_2 and 0.1003 gram H_2O.

	Calculated for $C_7H_{12}O_2N_2$.	Found.
C	53.25	53.44
H	7.70	7.79

The optical rotation was observed in normal caustic soda solution.

$c = 1.925$, $l = 2.20$, $\alpha = -2°.83$, hence $[\alpha]_D^{20} = -68°.2$.

After five hours the value for α had fallen to −1°.0, after 16 hours to −0°.20, while after 30 hours the solution was optically inactive.

i-α-*Uramidoisobutylacetic Acid.*—This substance was obtained from synthetic optically inactive leucine by the same method as that employed in the case of the active substance. The inactive uramido acid appears to be slightly more soluble in water than the active isomer and crystallizes from water in small platelets, which frequently arrange themselves in such a fashion that to the unaided eye they have the appearance of needles. After repeated crystallization from water the substance melts at 206°–208°.

Analysis:

0.1481 gram substance gave 0.2610 gram CO_2 and 0.1032 gram H_2O.

0.1851 gram substance gave 0.02968 gram nitrogen.

	Calculated for $C_7H_{14}O_3N_2$.	Found.
C	48.28	48.13
H	8.04	7.74
N	16.09	16.03

i-*Isobutylhydantoin.*—This substance was obtained by boiling the inactive uramido acid with ten parts of ten per cent. hydrochloric acid and also by acidifying the alkaline solutions of the active hydantoin after they had stood for several days at the ordinary temperature and had become entirely optically inactive. The products from the two different sources showed no difference in properties. The substance crystallizes from water, in which it is moderately soluble, in needles which, after repeated crystallization, melt at 211°–214°.

Analysis:

0.0964 gram substance gave 0.1904 gram CO_2 and 0.0709 gram H_2O.

	Calculated for $C_7H_{12}O_2N_2$.	Found.
C	53.85	53.75
H	7.70	8.17

l-*Parahydroxybenzylhydantoin.*—This substance has already been described under the incorrect name of tyrosinehydantoin. It was detected by Blendermann[1] in the urine of rabbits which had received very large doses of tyrosine, but the writer has shown in a paper which will appear shortly in the *Journal of Biological Chemistry* that the substance was probably produced by the interaction of excreted tyrosine and urea as a result of the method of urine analysis adopted by Blendermann. The substance has also been obtained by Lippich.[2] The following was found to be the most advantageous method of preparation: Pure *l*-tyrosine obtained from the hydroly-

[1] Z. physiol. Chem., **6**, 234.

[2] Ber. d. chem. Ges., **41**, 2973.

sis of proteins[1] is suspended in 10 parts of actively boiling water and solid potassium cyanate is added rapidly in small portions until the tyrosine is completely dissolved. Dilute sulphuric acid (1 : 4) is then added until the solution is strongly acid and the liquid is then boiled under a reflux condenser for half an hour. On cooling, the hydantoin separates out in the form of aggregates of white needles. The yield is excellent. The melting point varies somewhat with the quantity of substance taken and with the speed of heating, but I have never found the variations to extend beyond the limits of 258°–263°. Using minute quantities of substance and heating moderately rapidly, the melting point is practically constant at 259°–262° (uncorr.). Blendermann, however, gives 275°–280° as the melting point, while Lippich records 242°–245° without commenting on the higher value of Blendermann.

Analysis:

0.1666 gram substance gave NH_3 = 0.02275 gram N.

	Calculated for $C_{10}H_{10}O_3N_2$.	Found.
N	13.59	13.66

The rotation was observed in normal sodium hydroxide solution and showed a steadily diminishing normal value on standing.

$\alpha = -5°.35$, $l = 2.0$, $c = 1.866$, hence $[\alpha]_D^{20} = -143°$.

After 2.5 hours the value of α had fallen to about half and after 17 hours the solution was entirely inactive.

i-*Parahydroxybenzylhydantoin.*—The inactive substance we obtained from racemic tyrosine by the same method as that employed in the case of the active substance. It was also obtained by acidifying the alkaline solution of the active compound after complete loss of optical activity, and lastly it was also obtained by mixing equivalent quantities of the *d* and *l* compounds and recrystallizing from water. It was possible to carry out the last experiment only on a small

[1] The specimen used was obtained from the autolysis of kidney cell-juice. The specific rotation in 4 per cent. hydrochloric acid was —12°.5.

scale, owing to the difficulty in obtaining the dextro compound. A small amount was obtained from certain animal experiments, to be described shortly in the *Journal of Biological Chemistry*. The inactive hydantoin melts at 258°–260° (uncorr.). When prepared from racemic tyrosine the product tended to crystallize in nodular aggregations of prisms, whereas the other preparations crystallized in the form of platelets.

Analysis:

0.1822 gram substance gave 0.3889 gram CO_2 and 0.0818 gram H_2O.

0.1763 gram substance gave NH_3 = 0.02394 gram N.

	Calculated for $C_{10}H_{10}O_3N_2$.	Found.
C	58.25	58.21
H	4.85	4.99
N	13.59	13.58

l-*Hydantoinacetic Acid.*—In order to obtain this substance *l*-aspartic acid (5.0 grams), potassium cyanate (6.0 grams) and water (25 cc.) were evaporated on the water bath. The residue was dissolved in excess of dilute (10 per cent.) hydrochloric acid and after boiling for 15 minutes the filtered solution was concentrated to about 25 cc. and allowed to crystallize in an ice chest. The *l*-hydantoinacetic acid, which is sparingly soluble, slowly crystallizes out and is purified from any contamination with potassium salts by recrystallization from water. The substance forms large, thick, highly refractive prisms, which begin to sinter at about 212° and melt at 220°–225°. The same substance has been obtained by Grimaux[1] by heating aspartic acid and urea and by Lippich by heating α-uramidosuccinic acid with hydrochloric acid. These authors record slightly lower melting points, but this may be due to admixture with the racemic compound. The specific rotation was determined in normal caustic soda solution:

$$\alpha = -13°.12,\ l = 2.2,\ c = 4.781,\ [\alpha]_D^{19} = -125°.$$

After six hours the value of α had fallen to about half the

[1] Bull. Soc. Chim., [2] **24**, 337, and Compt. Rend., **81**, 325 (1875).

original value, after eleven hours it was reduced to one-quarter, while at the end of thirty hours the solution was no longer optically active. The specific rotation varies with the concentration of both substance and alkali. The specific rotation of 0.988 per cent. solutions in 0.25 N caustic soda, ammonia and baryta were found to be —141°, —131° and —131°, respectively. As was mentioned in the introduction, these solutions underwent racemization at different rates. The baryta solution became inactive after about 42 hours, followed by the caustic soda solution in about 55 hours, while the ammonia solution required about 90 hours. The temperature varied from 18°–20° throughout the observations.

l-Hydantoinacetic Acid.—On acidifying and concentrating the solutions of the laevo compound in caustic soda after the optical activity had vanished, crystals of the inactive compound were readily obtained. The substance resembles the laevo compound closely, but melts at a slightly higher temperature, 225°–228°, first slightly sintering. The substance crystallizes in large, highly refractive prisms.

Analysis:

0.1688 gram substance gave 0.2382 gram CO_2 and 0.0608 gram H_2O.

	Calculated for $C_5H_6O_4N_2$.	Found.
C	37.98	38.49
H	3.80	4.00

l-Hydantoinpropionic Acid.—The compound was obtained from *d*-glutamic acid (10.0 grams) and potassium cyanate (7.0 grams) by the same method as was employed for the *l*-hydantoinacetic acid. The substance is somewhat more soluble in water than its homologue and has a marked tendency to form supersaturated solutions. It crystallizes from water in large prismatic needles melting at 179°–181°.

Analysis:

0.3229 gram substance, dried at 100°, gave 0.4927 gram CO_2 and 0.1386 gram H_2O.

	Calculated for $C_6H_8O_4N_2$.	Found.
C	41.86	41.61
H	4.65	4.77

The specific rotation in aqueous solution underwent no change on standing for 3 days at 20°.

$\alpha = -3°.05$, $c = 2.00$, $l = 2.2$, hence $[\alpha]_D^{20} = -50°.0$.

The specific rotation in normal caustic soda was higher than in water and the value of α steadily diminished on standing.

$\alpha = -6°.95$, $c = 4.00$, $l = 2.2$, hence $[\alpha]_D^{23} = -79°$.

The rotation of a 2.26 per cent. solution in normal caustic soda fell to one half in 3.5 hours and the solution was entirely inactive after 18 hours.

i-*Hydantoinpropionic Acid.*—On acidifying the alkaline solutions of the active variety of this substance after optical activity had vanished, and concentrating, the inactive hydantoin was readily obtained. It crystallized in large, well-formed, transparent prisms which melt sharply at 167°–169°. In all respects save that of optical activity this substance closely resembles its laevorotatory isomer.

d-*Methylethylhydantoin.*—A small quantity of *l*-methylethylaminoacetic acid (*l*-isovalin) most kindly presented by Dr. Felix Ehrlich served for the preparation of this hydantoin. The amino acid, which had been obtained by the resolution of the inactive acid by Ehrlich's yeast method,[1] was converted into the sparingly soluble methylethyluramidoacetic acid by warming with potassium cyanate and precipitating with hydrochloric acid. The uramido acid, on account of the small amount available, was not recrystallized but was at once converted into the hydantoin by evaporation with 5 per cent. hydrochloric acid. The hydantoin was a sparingly soluble substance, crystallizing in transparent prisms, melting at 172°–173°.

Analysis:

0.1338 gram substance gave NH_3 = 0.0287 gram N.

	Calculated for $C_5H_{10}O_2N_2$.	Found.
N	21.54	21.45

[1] Biochem. Z., **8**, 438.

The substance was dextrorotatory in normal caustic soda solution and the value of α showed no change after standing for four days. The actual value for the specific rotation cannot be stated with accuracy, since there is no guarantee that the laevorotatory amino acid from which it was prepared was free from the inactive acid.[1] The rotation observed was as follows:

$$\alpha = +0°.81,\ l = 2.0,\ c = 1.247,\ [\alpha]_D^{20} = +32°(?).$$

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THE FRIEDEL AND CRAFTS REACTION WITH CHLORIDES OF UNSATURATED ACIDS.

BY E. P. KOHLER, G. L. HERITAGE AND M. C. BURNLEY.

The following investigation was undertaken in connection with the preparation of an extensive series of α,β-unsaturated ketones for the purpose of comparison by physical measurements. Many of these ketones are very easily obtained by the Schmidt-Claissen[2] condensation of an aldehyde with a saturated ketone; but with aliphatic aldehydes, and with aromatic aldehydes in which the carbonyl group is in an aliphatic side chain, the method generally gives aldols from which water is eliminated with difficulty, or else complex products not closely related to unsaturated ketones. We decided, therefore, to ascertain to what extent the Friedel and Crafts reaction can be used for preparing such ketones. The investigation led to the discovery of a number of facts of general interest in connection with the Friedel and Crafts reaction. These are published in this paper.

The literature on the subject under investigation is meager. The reaction was first applied to unsaturated chlorides by Stockhausen and Gattermann[3] in 1892. These investigators started with the chlorides of cinnamic and phenylpropiolic acids, and obtained an excellent yield of the expected unsat-

[1] The methylethylaminoacetic acid employed possessed a specific rotation of —9°.1 in 5 per cent. aqueous solution.

[2] Ber. d. chem. Ges., **13**, 2342.

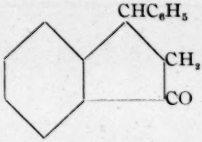
[3] *Ibid.*, **25**, 3536.

urated ketone when they used anisol or phenetol, but could isolate no solid products when they used aromatic hydrocarbons. They attributed this result to the difference in the reactivity of phenol ethers and hydrocarbons.

Many years later Moureu[1] studied the reaction between the chloride of acrylic acid and benzene in the presence of aluminium chloride. He isolated a small quantity of a solid product that he assumed to be vinylphenyl ketone, but which was, in reality, α-hydrindone. It was shown, a few years ago, that a satisfactory yield of unsaturated ketone can be obtained both with crotonyl chloride and benzene[2] and with cinnamyl chloride and mesitylene.[3]

We have found that the reaction between cinnamyl chloride and benzene takes place almost as readily as that between the same chloride and phenol ethers, but the product is a mixture of two saturated ketones—diphenylpropiophenone and phenylhydrindone:

I. $C_6H_5CH:CHCOCl + 2C_6H_6 = (C_6H_5)_2CHCH_2COC_6H_5 + HCl$;

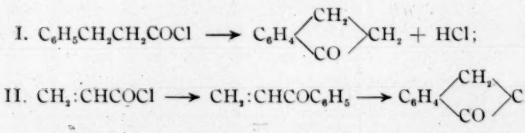
II. $C_6H_5CH:CHCOCl + C_6H_6 =$  $+ HCl$.

A reaction between crotonyl chloride and benzene, similar to that represented by the first equation, was described in an earlier paper. It was there pointed out that such a result might be due either to the addition of hydrogen chloride to the unsaturated ketone first formed, and subsequent reaction with a second molecule of benzene, or to 1,4-addition of an organic aluminium compound to the same unsaturated ketone. We have not succeeded in getting any conclusive evidence in favor of either of these mechanisms.

The reaction expressed by the second equation represents a new indene synthesis which differs from that devised by

[1] Ann. Chim. Phys., [7] **2**, 198.
[2] This Journal, **42**, 375.
[3] *Ibid.*, **38**, 510.

Kipping in that a benzene nucleus introduced by means of the Friedel and Crafts reaction, and not one already present in the acid chloride, forms the foundation of the bicyclic system. The difference is illustrated by the following equations, which represent the synthesis of α-hydrindone:

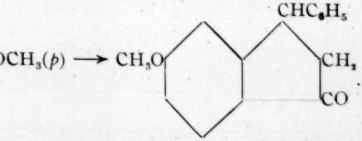


The difference in the results obtained when cinnamyl chloride is condensed with benzene and with anisol may be due, in part, to the greater reactivity of phenol ethers, as assumed by Stockhausen and Gattermann; but this is certainly not the principal factor. With crotonyl chloride and benzene it is possible to conduct the reaction so as to get, at will, either saturated or unsaturated ketone. In concentrated solutions and at low temperatures the product is the unsaturated ketone, because, under these conditions, the aluminium chloride derivative of this ketone is so sparingly soluble that it separates quickly and thus escapes further reaction. In more dilute solutions and at a higher temperature the aluminium chloride derivative remains in solution long enough to react with a second molecule of benzene, and this process takes place so readily that when only one equivalent of benzene is used nearly half of the acid chloride is left unchanged. The determining factor in this case is, therefore, the solubility of the aluminium chloride derivative of the unsaturated ketone.

The reactions with cinnamyl chloride cannot be controlled like those with crotonyl chloride because the double compound between the acid chloride and aluminium chloride is so slightly soluble that it is necessary to use higher temperatures and more dilute solutions. Phenol ethers give unsaturated ketones, nevertheless, because the alkoxyl groups hinder or prevent the secondary reactions that lead to saturated compounds. Thus indene synthesis does not take place

because this would necessitate closure of the second ring in the meta position with reference to alkoxyl:

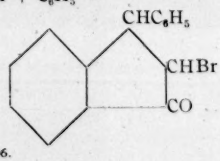
$C_6H_5CH:CHCOCl + C_6H_5OCH_3 = C_6H_5CH:CHCOC_6H_4OCH_3(p)$;

$C_6H_5CH:CHCOC_6H_4OCH_3(p) \longrightarrow$ 

Our experiments show that the secondary reaction involving addition of a molecule of phenol ether to the unsaturated ketone first formed is likewise impossible—probably owing to the stability of the double compounds that alkoxy ketones, as well as phenol ethers, form with aluminium chloride. For similar reasons it is just as easy to get unsaturated ketones by using mesitylene as it is by using phenol ethers.

These results showed that the Friedel and Crafts reaction can be used in exceptional cases only for making α,β-unsaturated ketones. As these substances are easily made by removing bromine from α,β-dibrom ketones, we also made some experiments for the purpose of determining to what extent these can be made by condensing the chlorides of α,β-dibrom acids with aromatic hydrocarbons.

Collet[1] added aluminium chloride to a solution of α,β-dibromhydrocinnamyl chloride in benzene, and obtained a solid, melting at 86°, which he assumed to be benzalacetophenone dibromide. We obtained the same product, but found that Collet had misinterpreted the reaction. The substance contains but one atom of bromine. As it gives *o*-benzoylbenzoic acid on oxidation, it must be an indene derivative formed according to the equation:

$C_6H_5CHBrCHBrCOCl + C_6H_5 =$ 

$+ HCl + HBr.$

[1] Compt. Rend., **125**, 306.

Similar products were obtained when the same acid chloride was used with other aromatic compounds. The yield was poor in all cases because aluminium chloride attacks the acid chloride itself at the lowest temperature at which it is possible to carry out the reactions.

With chlorides of the corresponding dibrom aliphatic acids, however, the Friedel and Crafts reaction gives an excellent yield of dibrom ketones.

EXPERIMENTAL PART.

Cinnamyl Chloride and Benzene.—In the first experiments equimolecular quantities of chloride and hydrocarbon were dissolved in carbon bisulphide and treated with aluminium chloride, but we found that the product always contained a large quantity of unchanged chloride. This was the case, also, when the acid chloride was first transformed into the Perrier double compound with aluminium chloride and this treated with one molecule of benzene dissolved in carbon bisulphide. In all subsequent experiments the hydrocarbon was, therefore, used in excess. The reaction was studied under the following conditions:

1. In carbon bisulphide cooled in a freezing mixture (—20°). No perceptible reaction took place in the dark. In direct sunlight the aluminium chloride dissolved, then the Perrier double compound separated in small yellow crystals which redissolved, very slowly, with evolution of hydrochloric acid.

2. In carbon bisulphide at the ordinary temperature. The aluminium chloride dissolved with brisk evolution of hydrochloric acid and the reaction was complete after the addition of slightly more than one molecule of aluminium chloride.

3. The double compound between cinnamyl chloride and aluminium chloride was made in carbon bisulphide, the solvent removed by decantation and the crystalline solid covered with benzene. The reaction that started in the dark was completed in the sunlight.

The orange-colored liquids obtained in these reactions were poured into iced acid, the organic products extracted with ether, and the extracts washed with sodium carbonate

and dried. The yellow liquids left after removal of the solvents in no case contained benzalacetophenone, for while they reduced potassium permanganate they did not combine with bromine. After standing in an ice chest for several days, the residue obtained by the first procedure partially solidified. The solid was purified by crystallization from methyl alcohol, from which it separated in large colorless prisms, melting at 78°.

Analysis:

0.1217 gram substance gave 0.3858 gram CO_2 and 0.0657 gram H_2O.

	Calculated for $C_{15}H_{12}O$.	Found.
C	86.6	86.4
H	5.8	5.9

As the substance has the composition and melting point of a ketophenylhydrindene previously obtained by the action of aluminium chloride on β,β-diphenylpropionyl chloride, it was compared with a preparation made in this way and thus identified as 3-keto-1-phenyl-2,3-dihydroindene.

A second product of the reaction was obtained by dissolving the residue from the indene derivative in petroleum ether and cooling the solution in a freezing mixture. After purification this was easily recognized as β,β-diphenylpropiophenone, which melts at 96°.

The filtrates from ketophenylhydrindene and diphenylpropiophenone contained a substance that decolorized a cold solution of permanganate in acetone, but no solid product could be isolated. The solvents were, therefore, removed and the residual liquid heated under diminished pressure; it lost hydrochloric acid freely above 150°, and gave a distillate in which benzalacetophenone was recognized by transformation into its dibromide. This result indicated the presence of β,β-chlorphenylpropiophenone in the original product and in all subsequent experiments this substance was isolated by adding to the residues a crystal of a preparation made by direct addition of hydrogen chloride to benzalacetophenone.

All methods of procedure gave variable amounts of the

same three products: ketophenylhydrindene, diphenylpropiophenone and chlorphenylpropiophenone. The presence of a small quantity of the halogen compound is easily explained because it results from direct addition of hydrochloric acid to benzalacetophenone. A number of experiments were made for the purpose of discovering the mechanism by which the other products are formed, but the results are inconclusive. The total amount of these two products formed in any experiment could be estimated with considerable accuracy because they were the only indifferent substances left after the halogen ketone had been destroyed with permanganate. They always constituted 93–95 per cent. of the entire product; but the relative amounts of the two varied within wide limits in experiments in which the conditions were intended to be as nearly as possible the same. Neither was obtained in more than insignificant quantities in all attempts at condensing benzalacetophenone or chlorphenylpropiophenone with benzene in the presence of aluminium chloride.

Cinnamyl Chloride and Brombenzene.—The reaction was carried out in carbon bisulphide at 0°. In one case ground aluminium chloride was added, in small quantities, to a solution containing cinnamyl chloride and excess of brombenzene, and in another excess of brombenzene was added, gradually, to a suspension of the double compound between cinnamyl chloride and aluminium chloride, but the result of both experiments was essentially the same. The solvent and the excess of brombenzene were removed by distillation with steam and the residual brown paste dissolved in boiling absolute alcohol. This solution, on cooling, deposited a solid that, after a few recrystallizations from alcohol, melted at 99°–100°.

Analysis:

0.1708 gram substance gave 0.3920 gram CO_2 and 0.0590 gram H_2O.

	Calculated for $C_{15}H_{11}OBr$.	Found.
C	62.71	62.58
H	3.83	3.84

The substance combined with bromine at —20° and rapidly reduced potassium permanganate, being oxidized to benzoic and *p*-brombenzoic acids. The same substance was readily obtained by adding a small quantity of aqueous potassium hydroxide to an alcoholic solution of equimolecular quantities of benzaldehyde and *p*-bromacetophenone. It is therefore *benzal*-p-*bromacetophenone*, $C_6H_5CH : CHCOC_6H_4Br$. The unsaturated ketone is readily soluble in alcohol, ether, and acetone; sparingly in ligroin. It separates from all of these solvents in pale yellow, friable plates that melt at 100°–101°.

The reaction with aluminium chloride gave only a small quantity of benzal-*p*-bromacetophenone, the largest yield not exceeding 25 per cent. of the possible quantity. The filtrates from this substance deposited a second product, which was purified by recrystallization from ligroin.

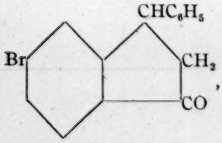
Analysis:

0.1332 gram substance gave 0.3053 gram CO_2 and 0 0463 gram H_2O.

	Calculated for $C_{15}H_{11}OBr$.	Found.
C	62.75	62.5
H	3.83	3.9

The substance is isomeric with benzalbromacetophenone, but neither reduces permanganate nor combines with bromine. It is, therefore, the corresponding indene derivative.

6-Brom-3-keto-1-phenyl-2,3-dihydroindene,



, is readily soluble in all common organic solvents. It separates from alcohol and from ether in prisms, from ligroin in large, lustrous plates. It melts at 60°–61°. The yield was 30 to 35 per cent. of the possible quantity.

Cinnamyl Chloride and Phenol Ethers.—The experiments of Stockhausen and Gattermann with anisol and phenetol

were repeated under different conditions, but no substance of the type of ketophenylhydrindene and diphenylpropiophenone could be detected in the products; excess of phenol ether does not affect the result in any way and higher temperatures simply lead to decomposition products of the unsaturated ketone. A similar result was obtained with cinnamyl chloride and diphenyl ether. This reaction takes place very slowly, even in direct sunlight, but the yield of unsaturated ketone is excellent, because the aluminium chloride derivative is very sparingly soluble in carbon bisulphide.

*Benzal-*p-*phenoxyacetophenone*, $C_6H_5CH:CHCOC_6H_4OC_6H_5$, is readily soluble in ether and acetone, moderately so in alcohol, sparingly in ligroin. It crystallizes in pale yellow plates that melt at 85°.

Analysis:

0.1571 gram substance gave 0.4794 gram CO_2 and 0.0736 gram H_2O.

	Calculated for $C_{21}H_{16}O_2$.	Found.
C	83.97	84.34
H	5.36	5.47

*β,β-Diphenyl-*p-*phenoxypropiophenone*, $(C_6H_5)_2CHCH_2COC_6H_4OC_6H_5$.—The reaction between phenylmagnesium bromide and benzalphenoxyacetophenone is similar to that between the same reagent and benzalacetophenone; the sole product is a saturated ketone resulting from 1,4-addition. The substance was purified by recrystallization from acetone and alcohol, from which it separated in needles melting at 103°.

Analysis:

0.2107 gram substance gave 0.6604 gram CO_2 and 0.1137 gram H_2O.

	Calculated for $C_{27}H_{22}O_2$.	Found.
C	85.71	85.48
H	5.82	5.99

The ketone is readily attacked by bromine but the action of this reagent is not, as usual, confined to the hydrogen in the α position. Thus, when one molecule of bromine was

added to one of the ketone dissolved in warm chloroform, the solid that separated was found to be a mixture of mono- and dibrom substitution products. A partial separation of the mixture was accomplished by extraction with cold chloroform. The more soluble component, after repeated recrystallization from a mixture of chloroform and alcohol, separated in needles melting at 163°–165°.

Analysis:

0.1582 gram substance gave 0.4072 gram CO_2 and 0.0597 gram H_2O.

	Calculated for $C_{27}H_{21}O_2Br$.	Found.
C	70.89	70.19
H	4.62	4.19

The bromine in this compound is in the aliphatic side chain because all of it can be removed by boiling with potassium hydroxide. The substance is, therefore, α-brom-β,β-diphenyl-*p*-phenoxypropiophenone.

The residue left after extraction with cold chloroform was recrystallized from boiling chloroform. It separated in minute needles melting at 211°–212°.

Analysis:

0.1287 gram substance gave 0.2845 gram CO_2 and 0.0461 gram H_2O.

	Calculated for $C_{27}H_{20}O_2Br_2$.	Found.
C	60.82	60.28
H	3.75	3.97

As only part of the bromine in this compound is eliminated by boiling with bases, the remainder must be located in a nucleus; it is probably in the *para* position of the phenoxyl group: $(C_6H_5)_2CHCHBrCOC_6H_4OC_6H_4Br$.

Experiments with Phenyldibrompropionyl Chloride.

Preparation of the Chloride.—We found the method of preparation used by Collet—addition of bromine to cinnamyl chloride—unsatisfactory, because it is extremely difficult to get a product free from unsaturated chloride in this manner. We therefore added bromine to cinnamic acid in the

usual way, suspended the dibromide in phosphorus oxychloride and gradually added a slight excess of phosphorus pentachloride. The resulting chloride could not be distilled without decomposition, but the chlorides of phosphorus were easily removed by heating to 150°–160° under diminished pressure. The colorless solid obtained in this way can be purified by crystallization from dry carbon bisulphide and ligroin but we found that, in our experiments, the crude and pure preparations gave the same results.

Action of Aluminium Chloride.—Our preliminary experiments showed that reactions with phenyldibrompropionyl chloride are accompanied by liberation of bromine. We therefore studied the behavior of this substance in the presence of aluminium chloride alone. For this purpose one molecule of aluminium chloride was gradually added to a solution of the acid in carbon bisulphide that was cooled in a freezing mixture. A slow but steady evolution of gas commenced almost immediately and the color of the solution soon showed the presence of free bromine. The evolution of gas continued for about 24 hours, during which the temperature was allowed to rise, very gradually, to 15°. Repeated analyses of the gas showed that, at all stages of the reaction, it consisted of hydrobromic acid mixed with a little hydrochloric acid.

The product of the reaction was poured into iced acid, separated, washed, and dried in the usual way. The ethereal solution was then distilled from a water bath, first under ordinary pressure and finally under 12 mm. The distillate contained, besides carbon bisulphide and ether, a small quantity of phenylacetylene—identified by its copper derivative—and a somewhat larger quantity of bromstyrene recognized by its odor and boiling point. The yellow residue was digested with cold ether. This left a considerable quantity of a sparingly soluble acid, which was purified by recrystallization from boiling acetone and thus obtained in long colorless needles, melting at 255°.

Aalysis:

I.no. 1799 gram substance gave 0.3134 gram CO_2 and 0.0481 gram H_2O.

II. 0.1471 gram substance gave 0.2564 gram CO_2 and 0.0376 gram H_2O.

	Calculated for $C_9H_7O_2Br$.	Found. I.	II.
C	47.57	47.51	47.53
H	3.08	2.97	2.84

The sodium salt of the acid was readily oxidized with aqueous permanganate and gave a new acid which melted at 251° and was identified as *p*-brombenzoic acid by comparison with a specimen on hand. The unsaturated acid was therefore *p*-bromcinnamic acid, previously made by Gabriel who gives the melting point 253°.

The filtrates from the *p*-bromcinnamic acid, on dilution with ligroin, deposited a mixture of acids that was finally separated into cinnamic acid, about 20 per cent., α-bromcinnamic acid, about 50 per cent., and a small quantity of a new acid that separated from benzene in stout prisms that melted at 172°.

Analysis:

I. 0.1733 gram substance gave 0.2552 gram CO_2 and 0.0422 gram H_2O.

II. 0.1423 gram substance gave 0.2127 gram CO_2 and 0.0327 gram H_2O.

	Calculated for $C_9H_8O_2ClBr$.	Found. I.	II.
C	40.98	40.22	40.75
H	3.03	2.70	2.54

The acid has the composition and chemical properties of an α-brom-β,β-phenylchlorpropionic acid; it gives benzoic acid on oxidation with potassium permanganate, α-bromcinnamic acid and potassium chloride when boiled in alcoholic solution with potassium acetate, and α-brom-β-phenyllactic acid when digested with hot water. The acid is different, however, from the known substance of this composition and structure; it melted 10° lower and a mixture of the two began to melt 20° to 25° below the lower melting component. The ether-ligroin from which all acids had been removed by extraction with sodium carbonate left, after evaporation, a

small quantity of nonacid substances that were not identified.

These results show that aluminium chloride removes both hydrobromic acid and bromine from phenyldibrompropionyl chloride and that action takes place slowly even at the temperature of a freezing mixture. The effect must be due to the phenyl group in the β position, because dibrompropionyl chloride forms a double compound with aluminium chloride which is perfectly stable at the ordinary temperature.

Phenyldibrompropionyl Chloride and Benzene.—After trying various methods of procedure, we adopted the following: Sixty grams of ground aluminium chloride were added to a solution of 121 grams of the acid chloride and 50 grams of benzene in 250 cc. of carbon bisulphide. The mixture was kept at —20° for 24 hours and then poured into iced hydrochloric acid. The carbon bisulphide layer, on evaporation, deposited a solid that was purified by recrystallization from absolute alcohol. It gave 63 grams of a substance that separated in very pale yellow needles melting at 89°–90°. This is evidently the product that had previously been obtained from the same reaction by Collet. Our analysis shows, however, that it is not phenyldibrompropiophenone:

0.1879 gram substance gave 0.4295 gram CO_2 and 0.0646 gram H_2O.

	Calculated for $C_{15}H_{11}OBr$.	Found.
C	62.71	62.33
H	3.83	3.76

The molecular weight was determined in boiling acetone ($K = 1710$).

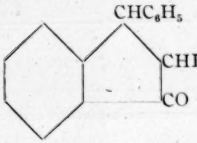
Solvent. Grams.	Substance. Grams.	Elevation of boiling point.	Molecular weight.
42.53	0.6274	0.089	285
42.53	1.1752	0.153	285
42.53	1.4925	0.202	262

Calculated for $C_{15}H_{11}OBr$, 287

The substance slowly reduced a solution of potassium permanganate in boiling acetone. The sole organic oxidation product was *o*-benzoylbenzoic acid, which was identified by

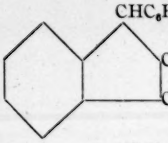
an analysis, by the melting points of the hydrous and anhydrous acids (90° and 120°), and by the melting point of the oxime, 162°.

These results prove that the substance is an indene derivative, the oxidation taking place in accordance with the equation:

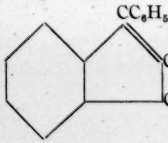


$$+ 4O = C_6H_5COC_6H_4CO_2H + HBr + CO_2.$$

2-Brom-3-keto-1-phenyl-2,3-dihydrindene reacts readily with organic and inorganic bases, and also with potassium acetate, but it is difficult to isolate pure substances from the products. The substance is most easily identified by means of the semicarbazone obtained by adding an aqueous solution of semicarbazide hydrochloride and potassium acetate to an alcoholic solution of the ketone:



$$+ NH_2CONHNH_2.HCl + 2CH_3CO_2K =$$



$$+ KCl + KBr + 2CH_3CO_2H.$$

Analysis:

0.1378 gram substance gave 0.3675 gram CO_2 and 0.0645 gram H_2O.

	Calculated for $C_{16}H_{13}ON_3$.	Found.
C	73.0	72.77
H	4.9	5.20

The unsaturated semicarbazone separates in minute yellow needles which, after recrystallization from alcohol and acetone, melt, with decomposition, at 212°. The same substance is formed when the yellow oil, obtained by boiling the halogen compound with alcoholic potassium hydroxide, is treated with semicarbazide.

Phenyldibrompropionyl Chloride and Brombenzene.—The reaction takes place much more slowly than the corresponding reaction with benzene and consequently leads to the formation of a larger quantity of acid by-products due to the interaction of the acid chloride and aluminium chloride. These acid products were removed by extraction with sodium carbonate. The extracted solution, on dilution with ligroin, deposited a solid which, after repeated crystallization from chloroform and absolute alcohol, melted at 143°–144°. The substance crystallizes in colorless needles, sparingly soluble in ether and alcohol, readily in acetone.

Analysis:

0.1518 gram substance gave 0.2762 gram CO_2 and 0.0358 gram H_2O.

	Calculated for $C_{15}H_{10}OBr_2$.	Found.
C	49.18	49.55
H	2.70	2.66

The bromine compound reduces potassium permanganate dissolved in acetone—slowly at the ordinary temperature, rapidly near the boiling point of acetone. The sole organic oxidation product is *p*-brom-*o*-benzoylbenzoic acid. This was purified by crystallization from methyl alcohol. It separated in large flat needles or plates melting at 174°.

Analysis:

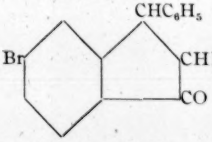
0.1540 gram substance gave 0.3109 gram CO_2 and 0.0436 gram H_2O.

	Calculated for $C_{14}H_9O_3Br$.	Found.
C	55.08	55.06
H	2.96	3.14

These results prove that the principal product of the reaction between phenyldibrompropionyl chloride and brom-

benzene is 2,6-dibrom-3-keto-1-phenyl-2,3-dihydroindene, an indene derivative with bromine in each nucleus:

$C_6H_5CHBrCHBrCOCl + BrC_6H_5 =$



$+ HCl + HBr.$

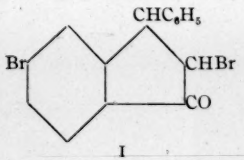
The filtrates from this compound contained another solid product that was isolated with difficulty but finally obtained in large colorless prisms, melting at 86°. This substance was readily soluble in acetone and ether, moderately in alcohol:

Analysis:

0.1834 gram substance gave 0.3334 gram CO_2 and 0.0409 gram H_2O.

	Calculated for $C_{15}H_{10}OBr_2$.	Found.
C	49.18	49.57
H	2.70	2.47

The substance is isomeric with the product melting at 143° and when oxidized with potassium permanganate it likewise gives brombenzoylbenzoic acid. The two are therefore either stereoisomers due to the presence of two unequal asymmetric carbon atoms, or structural isomers that differ in the position of the bromine atom in the second ring:



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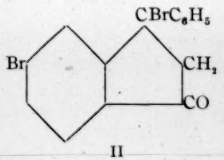
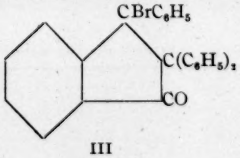


II



III

Only substances related in this way could be formed in the reaction with brombenzene and also give *p*-brom-*o*-benzoylbenzoic acid on oxidation. Formula II is, however, exceedingly improbable for either of the substances in question because, judging from the observations made with the corresponding triphenylindene derivative (III), the bromine in a compound with this structure would be as reactive as the bromine in triphenylbrommethane. This is not the case. It is much more probable, therefore, that the substances are stereoisomers (I). This conclusion is supported by the ease with which the higher melting is transformed into the lower melting substance by heating. A perfectly clean and almost complete transformation is obtained by keeping it at its melting point for an hour.

CHEMICAL LABORATORY,
BRYN MAWR COLLEGE.

THE EQUILIBRIUM BETWEEN AMMONIUM BENZOATE AND BENZAMIDE AND WATER.

BY E. EMMET REID.

Acetamide has long been prepared by distilling, or otherwise heating, ammonium acetate. Hofmann[1] prepared a number of aliphatic amides by heating the ammonium salts of the corresponding acids. He obtained yields running up to about 80 per cent., particularly for the amides of higher molecular weights. Menschutkin[2] and later Goldschmidt[3] studied the formation of anilides, both as to rate and limit. Both of these investigators concluded that the formation of anilides is analogous to esterification. Menschutkin found well-defined limits for the formation of the anilides and, in a later paper,[4] took up the question of the formation of amides. He prepared pure ammonium salts and heated specimens of these in sealed tubes and estimated the amount of ammonium salt remaining by titration of the acid of the ammonium salt in strong alcohol solution, in which ammonia does not

[1] Ber. d. chem. Ges., **15**, 977.
[2] *Ibid.*, **15**, 1615. J. prakt. Chem., [2] **26**, 208.
[3] Z. physik. Chem., **24**, 353.
[4] J. prakt. Chem., **29**, 422, 436.

affect phenolphthalein. He used ammonium salts of acids from formic to caproic and also benzoic and anisic acids. With the salts of the aliphatic acids good results were obtained, showing that a limit is reached in each case, that the limit varies somewhat with the temperature, and that it varies with the acid. At 155°, the limit rose rather regularly from 81.46 per cent. of amide for acetic acid, to 84.33 per cent. for caproic acid. He did not try the influence of excess of acid or of ammonia and did not make any attempt to reach the limit from the other end, that is, from a mixture of amide and water.

With the ammonium salts of benzoic and anisic acids he got almost no amide formation, ammonium benzoate giving him, at 155°, 6.70 per cent. of amide in 240 hours and 8.82 per cent. in 288 hours. His results, though excellent for the fatty acids, did not settle the question for the aromatic series.

In connection with a study of the esterification of benzamide by alcohol and mercaptan it became of interest to know the location of the corresponding limit with water, hence the following preliminary study was undertaken:

Materials.—The benzamide used was made from benzoyl chloride and ammonia. It was crystallized twice from water, once from alcohol, once from dilute ammonia, again from water, and finally from conductivity water. The ammonium benzoate was made from Kahlbaum's best benzoic acid and ammonia, and dried in the air. As it was found to lose ammonia and not to be constant in composition the ammonia content of each sample was determined. Conductivity water was used in the experiments with the amide.

Method of Work.—The benzamide and water, or the ammonium benzoate, as the case might be, were weighed into small hard glass tubes which had been well extracted with dilute hydrochloric acid before use. The mixture about half filled the tubes. They were heated exactly as in the experiments with benzoic acid and mercaptan.[1] After opening and breaking, the tubes and their contents were placed quickly in the stills. The ammonia was estimated by distillation with mag-

[1] This Journal, **43**, 489.

Table I.—Benzamide and Water.

Time in hours	41	41	60	64	64	64	64
Temperature	180–220°	180–220°	170–220°	200–220°	200–220°	200–220°	200–220°
Wt. amide	0.3633	0.3633	0.3633	0.4110	0.5439	0.3677	0.3904
Wt. water	0.0522	0.0868	0.1102	0.1019	0.1125	0.0548	0.0702
Amide (millimoles)	3.000	3.000	3.000	3.391	4.491	3.036	3.224
Water (millimoles)	2.897	4.817	6.115	5.656	6.245	3.042	3.897
Ammonia found (millimoles	0.792	0.950	1.169	1.085	1.243	0.757	0.866
Amide left (millimoles)	2.208	2.050	1.831	2.306	3.248	2.279	2.358
Water left (millimoles)	2.105	3.867	4.946	4.571	5.002	2.285	3.031
r	7.410	8.804	6.627	8.562	10.515	9.087	9.530
$\sqrt{r}$	2.722	2.967	2.574	2.926	3.243	3.015	3.087
Per cent. ammonium salt at limit	26.87	25.21	(27.98)	25.47	23.57	24.91	24.47

nesium hydroxide and allowance was made for the small amount of amide thus decomposed.[1] In the case of the ammonium benzoate samples, the amide remaining was estimated by decomposition with strong caustic soda. From the total ammonia thus found, the ammonium benzoate in the original sample was estimated and the balance of the sample considered as benzoic acid.

The results are given in the above table. The units are the same and the results were calculated according to the same plan as used in the above mentioned paper on benzoic acid and mercaptan.

In the third experiment the temperature for the last 19 hours was 170°–180°. This indicates that at lower temperatures the limit for the formation of amide from ammonium salt is lower.

The average, excluding the third experiment, is 25.17 per cent., which means that a mixture of equivalent amounts of benzamide and water, when heated to 200°–220°, is one-fourth transformed into ammonium benzoate, or that the initial rate of amide formation is nine times as great as that of its decomposition. Or writing the equation as reversible and using the notation introduced in the above mentioned paper on benzoic acid and mercaptan, we have:

$$C_6H_5CONH_2 + H_2O \underset{9}{\overset{1}{\rightleftharpoons}} C_6H_5COONH_4.$$

Table II.—Ammonium Benzoate.

Time in hours	70	70
Temperature	200–220°	200–20°
Original acid (millimoles)	2.898	2.787
Original ammonia (millimoles)	2.886	2.808
Acid at limit (millimoles)	0.674	0.715
Ammonia at limit (millimoles)	0.662	0.694
Benzamide-water(millimoles)	2.224	2.093
r	11.09	8.828
$\sqrt{r}$	3.245	2.971
Per cent. of ammonium salt at limit	23.56	25.18
Average		24.4

[1] THIS JOURNAL, **41**, 486.

These results, being in substantial agreement with those found starting from the other end, show that the reaction is strictly reversible and that the limit may be easily reached from either end. The variation of the individual results may be, in part, attributed to the fact that the temperatures were not regulated, for Menschutkin found a variation of the limit with a change of temperature. It will be noticed that the limit as found is substantially the same with varying proportions of the constituents.

Benzoic acid, contrary to Menschutkin's few observations, is shown to be in line with the acids of the aliphatic series. The rather low temperature at which he tried the ammonium benzoate may be the reason for his poor results on that salt.

JOHNS HOPKINS UNIVERSITY.
BALTIMORE, MD.,
April 28, 1910.

FRICTION IN THE BOMB CALORIMETER.

BY H. A. ROESLER.

The heating effect due to the friction of the stirrer in the bomb calorimeter is generally supposed to be very small, but in connection with some calculations relative to the rate of radiation in the calorimeter certain discrepancies were found which could only be explained by the addition of considerable heat from the friction of the stirring apparatus, and a method for determining this heating effect was therefore evolved.

The object of this article is to show how the heat of friction, its magnitude under different conditions, and its relation to the calculation of the radiation correction may be accurately determined.

The rise in temperature during the initial period is due to the algebraic sum of the heat absorbed or evolved by radiation and the heat added by the stirring apparatus.

Let S = rate of rise in temperature due to radiation plus friction.

V = rate of rise in temperature due to radiation alone.

F = rate of rise in temperature due to friction.

M = temperature of the calorimeter.

M' = temperature of the surrounding medium.

t = difference between the temperature of the calorimeter and that of the surrounding medium.

r = rate of rise in temperature per degree difference in temperature (t) due to radiation.

This value of r may be termed the radiation constant of the calorimeter. It is obtained by dividing the rate of rise in temperature by the difference in temperature of the calorimeter and the surrounding medium.

Then:

$$V = rt.$$

$$F = S - V = S - rt.$$

$$t = M' - M.$$

Two values of S, S_1 and S_2 are now determined at temperature differences t_1 and t_2. Then we have:

$$\frac{S_1 - S_2}{t_1 - t_2} = \frac{(V_1 + F) - (V_2 + F)}{t_1 - t_2} = \frac{V_1 - V_2}{t_1 - t_2}.$$

But since $\frac{V_1}{t_1} = r$ and $\frac{V_2}{t_2} = r$, then $\frac{V_1 - V_2}{t_1 - t_2} = r$.

Therefore,

$$F = S_1 - rt_1 = S_1 - \left(\frac{S_1 - S_2}{t_1 - t_2}\right) t_1.$$

The value of F is most accurately determined when one value of t is nearly zero and the other is several degrees above or below or when one is positive and the other negative.

A number of sets of determinations for S and t, one of which is shown below for the purpose of illustration, were made on the calorimeter used in this laboratory. The values for S were obtained by taking 10 consecutive readings at intervals of one minute and averaging. The temperature of the calorimeter was then raised about 0.5 of a degree by means of a small iron wire coil, immersed directly in the water and heated electrically, and S was again determined in the same manner. In order to keep conditions as nearly uniform as possible, the calorimeter is surrounded by a water jacket, a double lid

placed over the top and a felt covering one inch thick fitted over all. The stirrer is of the propeller type, the shaft, to which is attached the pulley, projecting out from the top of the calorimeter.

The results obtained are as follows:

Reference No.	Average, M'.	Average, M.	t.	Average, S.
1	23°.013	18°.544	4°.469	0°.0128
2	22°.987	19°.065	3°.922	0°.0112
3	22°.966	19°.576	3°.390	0°.0099
4	22°.947	20°.061	2°.866	0°.0089
5	22°.933	20°.556	2°.377	0°.0079
6	22°.928	21°.046	1°.822	0°.0067
7	22°.939	21°.504	1°.435	0°.0055
8	22°.943	21°.987	0°.956	0°.0047
9	22°.964	22°.525	0°.439	0°.0036
10	22°.980	22°.796	0°.184	0°.0029
11	22°.981	22°.825	0°.156	0°.0029
12	22°.996	23°.007	—0°.011	0°.0024
13	23°.006	23°.026	—0°.020	0°.0023
14	23°.016	23°.049	—0°.033	0°.0023

Taking various combinations of S and t and calculating F, we get:

Reference No.	F.	Reference No.	F.
1 and 14	0°.0024	3 and 14	0°.0024
1 and 13	0°.0023	3 and 13	0°.0023
1 and 12	0°.0024	3 and 12	0°.0024
1 and 11	0°.0025	3 and 11	0°.0026
1 and 10	0°.0025	3 and 10	0°.0025
1 and 9	0°.0026	3 and 9	0°.0027
2 and 14	0°.0024	4 and 14	0°.0024
2 and 13	0°.0023	4 and 13	0°.0023
2 and 12	0°.0024	4 and 12	0°.0024
2 and 11	0°.0026	4 and 11	0°.0026
2 and 10	0°.0025	4 and 10	0°.0025
2 and 9	0°.0026	4 and 9	0°.0026
		Average,	0°.0025

Thus F is found to be constant for almost any combination of S and t, provided the values for t are several degrees apart.

When F is calculated from the readings taken in an ordinary calorific determination the same result is obtained:

Lab. No.		Av. M'.	Av. M.	t.	S.	F.
26627	Initial period	20°.940	19°.319	+1°.621	+0°.0065	
	Final period	20°.950	22°.017	—1°.067	+0°.0000	0°.0026
26628	Initial period	21°.070	19°.577	+1°.493	+0°.0067	
	Final period	21°.115	22°.282	—1°.167	+0°.0000	0°.0029
26629	Initial period	21°.625	19°.865	+1°.760	+0°.0075	
	Final period	21°.655	22°.557	—0°.902	+0°.0002	0°.0027
26630	Initial period	21°.805	19°.655	+2°.150	+0°.0080	
	Final period	21°.830	22°.344	—0°.514	+0°.0012	0°.0026
26631	Initial period	20°.270	19°.620	+0°.650	+0°.0042	
	Final period	20°.320	22°.236	—1°.916	—0°.0022	0°.0026

The water equivalent of the calorimeter from which these data were taken is 2944 grams, therefore the friction was adding to the apparatus $2944 \times 0.0024 = 7.1$ calories per minute. During the whole combustion period of 6 minutes this would be $6 \times 7.1 = 42.6$ calories.

The value for F obtained on another calorimeter which was equipped with the Mahler stirrer was 0°.005. This instrument has a water equivalent of 2767 grams, which gives 13.8 calories per minute for friction or 82.8 calories for the whole combustion period.

This is much larger than would be suspected but it is taken into account in the correction for radiation, as shown below. It emphasizes, however, the necessity of having an absolutely uniform rate of stirring. The author found upon one occasion that even the loosening of the belt reduced the friction almost 50 per cent.

The best motor to employ is an alternating current induction fan motor. A direct current motor is not so desirable because changes in the voltage will also vary the speed. Stirring by hand should not be attempted if it is possible to obtain a motor, because experience has shown that it is impossible to stir continuously for 20 minutes and maintain a constant speed.

The relation of the friction to the correction for radiation may be shown as follows:

The formula used for the calculation of the radiation correction is that of Regnault-Pflaunder,

$$C = nV + \frac{V' - V}{\theta' - \theta}\left(\frac{\theta_0 + \theta_n}{2} + \sum_1^{n-1} \theta - n\theta\right),$$

where

n = number of minutes in the combustion period.

V = rate of rise in temperature during the initial period.

V' = rate of rise in temperature during the final period.

θ = mean temperature of the calorimeter during the initial period.

θ' = mean temperature of the calorimeter during the final period.

θ_1, θ_2 ..... θ_n = temperature at the end of the first, second ..... nth, minutes of the combustion period.

θ_0 = temperature at the moment of ignition.

In practice we do not get the values V and V', but $V + F$ and $V' + F$. If, then, these values be substituted in the formula in the place of V and V' we find that the value of C has been increased to that of $C + nF$. That is, we get the identical result which would be obtained if we used the true values of V and V' and then added to the value of C thus obtained the correction for the rise in temperature, nF, caused by the friction during the combustion period.

The magnitude of F does not, therefore, effect the accuracy of a calorific determination provided it is uniform throughout the whole time of the determination.

LABORATORY OF THE CONSOLIDATION
COAL CO., INC.

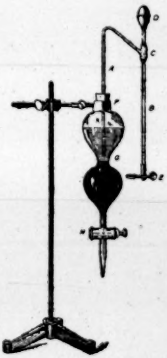
NOTE.

A SEPARATORY APPARATUS.

The accompanying cut illustrates a separatory apparatus which we find to be a valuable adjunct to our laboratory equipment. It consists of a double bulbed separatory funnel and a pipette siphon, the latter having been fully described in the June number of *The Journal of the American Chemical Society* of this year.

The advantages of this form of separatory funnel are: First,

it allows of a better and more rapid extraction, for upon inverting the funnel the solvent and solution must pass each other at the constriction *G*, thus permitting more intimate contact of the two liquids. Second, when it is desired to siphon off the top layer in the funnel, the surface of the last portions siphoned is reduced to that in the constriction, thus allowing a more perfect separation. Third, emulsions do not form so readily when the space is constricted like that at *G*, and when they do form, they are more easily destroyed than in the ordinary funnel. Fourth, when three layers are formed the middle layer may be completely removed by means of the siphon without disturbing the other two.



A cork is fitted to the branch *A* of the siphon so that its position may be raised or lowered during the process of siphoning. To operate the siphon: Open the spring clamp *E*, compress the rubber bulb *D*, close the lower end of *B* by releasing the pressure on the spring clamp, slowly release the pressure on the rubber bulb, and the liquid will be drawn into the siphon, filling both arms and part of the bulb *C*. Then open clamp *E* and the liquid siphons over.

When it is desired to filter the siphoned liquid, the two processes may be made to go on simultaneously, by supporting the filter so that the siphoned liquid will run into it, and holding open the spring clamp by means of a chip of wood, so that the drip from the siphon equals that from the filter.

The siphon may also be used to advantage for removing supernatant liquids where decantation is found to be impracticable, for drawing off standard solutions, reagents and liquids with offensive and poisonous vapors, etc.

NEVADA AGRICULTURAL EXPERIMENT STATION.

C. A. JACOBSON and
S. C. DINSMORE.

REPORT.

CHEMICAL CONSTITUTION AND THE ABSORPTION OF LIGHT.[1]

A Method of Chemical Analysis.

Research along many lines in science is often very much

[1] This report is based upon an article by H. Ley, entitled "Ueber die Beziehung zwischen Lichtabsorption und chemischer Konstitution bei organischen Verbindungen." See Jahrbuch der Radioaktivität und Elektronik, **6**, 274 (1909).

stimulated by the requirements of technology. This is especially true in connection with many branches of organic chemistry and a good example is furnished by the pure food laws. In regulating the use of various coloring and preserving matters added to foods, it is necessary that the examiners shall be able to recognize various compounds easily and quickly. Many organic compounds possess very characteristic colors and it has often been asked whether the absorption spectra of these compounds would aid in their analysis. Our present knowledge of absorption spectra is mostly limited to the visible region of the spectrum. Before this method of analysis can reach its full service to chemists it will be necessary to measure the absorption throughout the region of the infrared. At present the absorption spectra of a few potassium salts have been explored to regions of wave lengths as long as 0.1 mm. (Electromagnetic waves having wave lengths between 8000 m. and 6 mm. have been produced.)

The analysis of inorganic compounds is probably less hopeful, although the absorption spectra would often help to identify compounds. A great many of the inorganic cations show characteristic absorption in the visible portion of the spectrum and practically all have bands in the infrared. J. Formanek[1] has suggested that the presence of metals in metallic compounds of alkannin could be determined from the absorption spectra of these compounds. The following measurements of the absorption bands of the different compounds of alkannin show the effect of the metal upon the position of the bands:

	λ.	λ.	λ.
Uranium	6870	6315	....
Iron	6545	6030	....
Potassium	6387	5910	....
Cobalt	6370	5845	5405
Sodium	6337	5857	....
Barium	6281	5805	5395
Lithium	6210	5745	5340
Nickel	6192	5725	5320
Calcium	6147	5682	5276
Copper	5953	5515	5128
Aluminium	5857	5425	5048

The use of absorption and emission spectra has been very successful in studying the elements of the rare earths and has been very extensively applied by Crookes, Becquerel, Exner, Demarçay, and many others. An account of this work is

[1] Die qualitative Spectralanalyse anorganischer Körper.

given by Böhm.[1] Recently Urbain[2] has employed the phosphorescent spectra in the purification of compounds of europium, gadolinium, terbium, dysprosium, neoytterbium and lutecium.

Atomic Structure and Spectra.

The greatest interest lies, however, in the relation between chemical constitution and absorption or emission spectra. The relation between flame, spark and arc spectra and the chemistry of the emitters is not known. The source of spectra like that from the blue cone of a Bunsen burner, the Swan spectra, is at present a much mooted problem. It is probable that chemical reactions play an important rôle in the emission and absorption of spectra, and especially of band spectra. We usually think of most spectrum lines like D_1 and D_2 of sodium as coming from the metallic atoms. Fredenhagen[3] points out that under most conditions oxygen is present. In chlorine, hydrogen or fluorine flames, calcium, strontium, thallium, sodium, barium and copper emit spectra that are very different from those obtained when oxygen is present. Under these conditions thallium does not emit the characteristic green line and the lines D_1 and D_2 are completely absent. Work on the absorption of sodium, mercury, potassium and various other vapors show that the presence of foreign gases modifies the character of the absorption very much. Many believe that certain series or groups of lines are due to chemical reactions of various kinds.

Chemical reactions and processes of ionization and recombination are believed to place the atom or molecule in a peculiar condition, in which it can emit energy to the ether or absorb energy from it. Under ordinary conditions the atom does not seem capable of doing this. In sodium vapor, for instance, according to present theories only one atom in thousands is taking part in absorption at any one time. The problem as to how energy is transferred to and from matter is one of the most fundamental problems of science. A striking example of the fact that a few atoms under peculiar conditions have the power of absorbing an enormous amount of energy from the ether is exhibited by the iron absorption lines in the solar spectrum. An arc of carbon electrodes containing iron as an impurity emits enough iron vapor to absorb as much as the iron vapor in the sun. It is thus seen that an infinitesimal amount of iron in the very great atmosphere

[1] Die Darstellung der seltenen Erden, Leipzig, 1905.
[2] Le Radium, June, 1909.
[3] Physik. Z., Oct. 24, 1907.

of the sun is sufficient to absorb a large part of the energy emitted by the photosphere.

Our present theory of the mechanism of the absorption and emission of radiations is very simple. Light and heat are electromagnetic radiations and hence the emitter and the absorber must either be an electric charge or a magnetic pole. As free magnetic poles are unknown to us while free electric charges are known, this theory makes the electric charge the origin of all electromagnetic phenomena. At present no positive electric charges are known to be associated with portions of matter smaller than the hydrogen atom. On the other hand, negative electrons are known to be associated with masses only about one two-thousandth that of the hydrogen atom. As far as experiment shows, these electrons always have the same properties and the same charge (the charge is invariably considered as constant when e/m varies), no matter from what element they may come. It is for these reasons that the electron is made the basis of all electromagnetic theory and at present there are but few phenomena capable of any explanation which cannot be explained by this theory.

Electromagnetic radiations then have their origin in electric charges. Continuous spectra (as from hot metals) are due to free electrons and these apparently have very little connection with the chemical constitution of the metal molecules. Fine line and band spectra are apparently due to different systems of electrons within the atom and are greatly affected in intensity by the presence of neighboring atoms. The electrons of this type vibrate in definite frequencies that can be changed only very slightly by changing the external conditions.

The Absorption Spectra of Organic Compounds.

The Unit of this Absorption.—In discussions concerning the color of organic compounds it is customary to speak of the selective absorption as being due to certain ions or molecules. This is probably true in the infrared; the electric charges absorbing these long wave length radiations are probably associated with masses of molecular size. But in the visible and ultraviolet portions of the spectrum the value e/m of the absorbers is invariably of the same magnitude as that of the electron. Drude[1] has investigated a large number of organic compounds and shows that the absorber of all the shorter waves of the spectrum is the negative electron. Houstoun[2]

[1] Ann. Physik, **14**, 677, 726, 936, 961 (1904).
[2] Nature, May 20, 1909. P. Roy. Soc., **82**, A, 606 (1909).

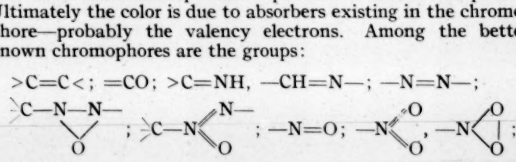
has calculated the value of $e/m = 1.297\ V\ K\ \frac{\lambda_1 - \lambda_0}{\lambda_0^3}$ for the absorption bands of several organic compounds and also shows that the absorber is the electron (V is the refractive index, K the maximum value of the coefficient of extinction; λ_0 is the wave length of maximum absorption, and λ_1 is the wave length for which the coefficient of extinction has a value equal to half its maximum. The formula used is based on the present theories of dispersion). The following table is from Houstoun:

Compound.	λ_0.	e/m.
Fuchsine in alcohol	5500	$1.8(10)^7$
Phloxin in water	5150	1.4 "
Crystal violet in alcohol	5750	4.9 "
Corallin in alcohol	4650	$1.6(10)^8$
Methylene blue in water	6650	5.4 "
Water blue in water	5750	8.1 "
Eosin in water	5150	6.9 "
Cyanine in alcohol	5870	5.8 "

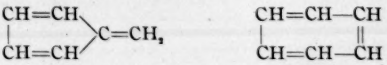
Throughout the present paper the absorbers are considered as negative electrons. These electrons have certain free periods corresponding to the bands of selective absorption. These free periods are greatly modified by the presence of certain chemical radicals and seem to be electrons that are situated either in the outer parts of the atom or between two or more atoms. Stark and others call these the valency electrons and consider that chemical valency is due to them. Chemical bonds will then be closely associated with the electric fields of these electrons. While the theory in its present state is confronted with many difficulties, yet it seems a step towards the explanation of the more or less vague chemical bond. As an aid to our imagination, we shall consider atoms or ions as large spherical regions throughout which a positive charge is uniformly distributed. These regions are sometimes spoken of as "spheres of influence." Two atoms collide when their "spheres of influence" touch. Groups of atoms composing ions, radicals or molecules, will have "spheres of influence." No ion can penetrate the sphere of influence of another atom or molecule. On the other hand, the electrons are very small and bear much the same relations in size to the atom that the sun bears to the solar system. The electric fields of the electrons occupy quite large volumes, however, although the energy of this field is mostly situated in a very small space. Electrons can therefore move through

ions and atoms if they have sufficient velocity. In most organic compounds it is considered that the valency electrons move in the interatomic spaces with considerable ease. In the metals a large number of the electrons are free. In organic compounds that are transparent to certain wave lengths, the electrons in general will be held within certain regions by forces which are supposed to be elastic in their nature.

The Theory of Chromophores.—In considering absorption spectra it is often quite sufficient to speak qualitatively of the color of different compounds. The introduction of certain groups into colorless compounds often results in a colored compound. Any such group is a chromophore. Sometimes the chromophore may be weak and it may require the addition of several chromophores to produce a colored compound. Ultimately the color is due to absorbers existing in the chromophore—probably the valency electrons. Among the better known chromophores are the groups:



The ethylene group, $>C=C<$, is a weak chromophore and several chromophores must be present before the absorption is sufficient to produce color. An example is that of fulvene and its isomer, benzene:

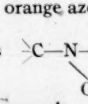
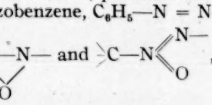


Fulvene. Benzene.

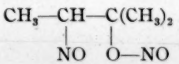
Benzene is colorless and exhibits absorption only in the ultraviolet, whereas fulvene is an orange-yellow.

The carbonyl group, $=C=O$, is also weak and several of the groups must be present in a compound to produce color. The following examples indicate how an increasing number of the carbonyl groups produces a greater and greater absorption of the shorter wave lengths:

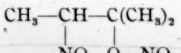
$R—CO—R$, colorless;
$CH_3—CO—CO—CH_3$, yellow;
$C_6H_5—CO—CO—C_6H_5$, yellow;
$CH_3—CO—CO—CO—CH_3$, orange.
$C_6H_5—CO—CO—CO—CO—C_6H_5$, red.

The combination of two phenyl groups causes absorption only in the ultraviolet. The introduction of the —CH = N— chromophore is sufficient to produce color, as is shown in the yellow benzylidenaniline, $C_6H_5CH = N—C_6H_5$. The azo chromophore, —N = N—, produces the same effect, as shown in the orange azobenzene, $C_6H_5—N = N—C_6H_5$. The chromophores  and  , on the other hand, are very weak.

The nitroso group, —N=O, is a very strong chromophore when it is joined to a carbon atom directly. The effect of this chromophore is shown in nitrosobenzene, $ON—C_6H_5$, which is of a green color. Wallach,[1] and recently J. Schmidt,[2] have investigated the following compounds, which are of a deep blue color:

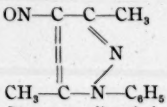


Alkylenenitrosite.

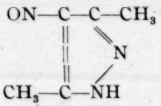


Alkylenenitrosate.

According to Wolff,[3] the following nitroso compounds, the first of which is green and the second blue, have the structures:

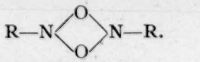


1-Phenyl-3.5-dimethyl-4-nitrosopyrazol.



3-5-Dimethyl-4-nitrosopyrazol.

The carrier of the color in these cases is the C—N=O group. Many of the aliphatic nitroso compounds show polymerization and are then often colorless. The polymerization of R—N=O to $(RNO)_2$ is probably accompanied by a rearrangement as follows:



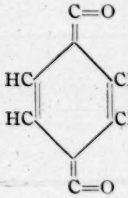
This would explain why the polymer is colorless.

[1] Ann. Chem. (Liebig), **241**, 288; **323**, 305.
[2] Ber. d. chem. Ges., **35**, 2323, 3721; **36**, 1768.
[3] Ann. Chem. (Liebig), **325**, 192.

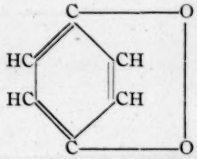
The nitro group or is a very weak chromophore. The aliphatic nitro compounds, CH_3NO_2, $C_2H_5NO_2$, etc., are colorless. When combined with other chromophores, colored compounds, such as nitrobenzene or nitronaphthalene, can be obtained. Stobbe[1] has investigated the influence of the nitro group on the fulgides. In solution the *p*-nitrophenylfulgide has a deep red color. The ortho and meta compounds are much less deeply colored.

Hantzsch[2] and Raschig[3] have shown that the $=N=O$ group acts as a chromophore in the sulphonate, $O=N=(SO_3K)_2$, which is violet in solution and orange in the solid state. The thiocarbonyl group, $=C=S$, is a rather strong chromophore. Examples are the blue compounds thioacetophenone, $C_6H_5—CS—CH_3$, and thiobenzophenone, $C_6H_5—CS—C_6H_5$. For a fuller account of the color properties of various compounds, the reader is referred to Ley's paper,[4] from which the data here recorded have been largely taken.

There has been a great deal of discussion whether quinone has the formula I or II:

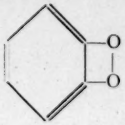


I.

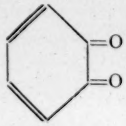


II.

Willstätter and F. Müller[5] have found that *o*-benzoquinone can exist in two forms, I and II, the former being colorless and the latter red:



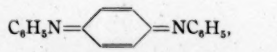
I.



II.

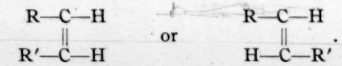
[1] Ber. d. chem. Ges., **38,** 4082 (1905).
[2] *Ibid.*, **38,** 2744.
[3] Dammer: Handb. d. anorg. Chem.
[4] Jahrb. d. Rad. u. Elek., **6,** 274–381 (1909).
[5] Ber. d. chem. Ges., **41,** 2580 (1908).

This fact may possibly explain several outstanding difficulties among quinone derivatives. It would be expected that the substitution of an (NR) group for oxygen in a quinone would give a deeply colored substance. As a matter of fact, quinonediphenylimide,



is brownish red. But the compounds NH : C_6H_4 : NH and O : C_6H_4 : NH are colorless. This can easily be explained if the latter compounds are assumed to have the superoxide formula similar to that of *o*-benzoquinone. The quinone chromophore enters into the composition of quite a large number of colored compounds.

The space relations of the chromophores seem to affect the color of compounds. For instance, the ethylene group can have two isomeric configurations:



This geometric isomerism may explain the following facts:

1. Diethoxynaphthostilbenes, C_2H_5O—$C_{10}H_6$.CH : CH.$C_{10}H_6$.OC_2H_5.[1] The form which has the highest melting point is colorless, while the lower melting form is yellow.

2. Dibenzoylethylenes, C_6H_5CO.CH : CH.COC_6H_5.[2] The higher melting form is colorless, while the lower melting form possesses a deep yellow color.

That the color producing power of the chromophores is due to the double bonds seems quite certain. When these bonds are saturated the resulting compounds are colorless.

Colored.

C_6H_5—N=N—C_6H_5, azobenzene.
C_6H_5—N=O, nitrosobenzene.
O = C_6H_4=O, quinone.
C_6H_5.CO.CO.CO.C_6H_5, diphenyltriketone.

Colorless.

C_6H_5NH—NHC_6H_5, hydrazobenzene.
C_6H_5—N.H.OH, phenylhydroxylamine.
HO.C_6H_4.OH, hydroquinone.
C_6H_5.CO.CH_2.CO.C_6H_5, dibenzoylmethane.

[1] Elbs: J. prakt. Chem., **47**, 72.
[2] Paal and Schulze: Ber. d. chem. Ges., **33**, 8795; **35**, 168.

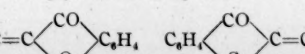
The different di- and tri-substitution products usually give rise to different absorption bands when the absorption is selective. Ortho- and metaxylene have one band, whereas paraxylene has two. The following gives the value of the limit of absorption when light is passed through a gram molecule of the substance.

	Cresol.	Dihydroxybenzene.	Hydroxybenzoic acid.
Meta	3433	3466	3359
Ortho	3413	3399	3080
Para	3359	3151	2986

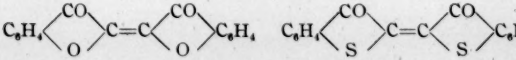
When a chromophore is introduced into a compound the bands may be shifted towards the red or towards the violet. The former effect is bathochromous, the latter hypsochromous. The effect of joining chromophores is usually bathochromous. For example:

	λ.	λ.	λ.	λ.
Benzene	2610	2540	2450	2440
Naphthalene	2850	2720	2630	2550
Anthracene	....	3600	3430	3280

In triphenylmethane the limit of the visible portion of the spectrum is reached. It may be stated here that anthracene and phenanthrene have entirely different absorption spectra, although the fluorescent spectra are very similar.[1] An auxochrome is a radical that causes the absorption to be more intense. An example is —CO—C=C—CO—, which appears in the indigos,



and also in the deeply colored compounds:



The groups CH_3, OCH_3, C_2H_5, the halogens, etc., are bathochromes, while the groups NO_2 and NH_2 are hypsochromes.

The infrared absorption spectra to about 15μ of a large number of organic compounds have been investigated by W. W. Coblentz.[2] Isomeric compounds are found to possess very different absorption, depending on the bonding of the atoms in the molecule. Stereomeric compounds, on the

[1] Elston: Astrophysical J., **25**, 3 (1907).
[2] Investigations of Infrared Spectra, Carnegie Publication No. 35.

other hand, were found to possess the same absorption spectra. The replacing of hydrogen by an NH_2 or CH_3 group usually results in the appearance of new bands. In the spectrum of certain benzene derivatives, however, the benzene spectrum is usually present. The carbohydrates investigated had characteristic spectra with absorption bands at 0.83 to 0.86μ; 1.67 to 1.72μ; 3.25 to 3.43μ; 6.75 to 6.86μ; and 13.6 to 14μ. The three isomeric xylenes have banded spectra in which the most important line in each group lies farthest toward the long wave lengths in the order ortho, meta, and para.

The author[1] has shown that the effect of the NO_3 group and of free nitric acid is hypsochromous, causing the uranyl bands to shift towards the violet. The effect of free hydrochloric acid or of zinc, aluminium or calcium chlorides on the uranyl chloride bands is bathochromous. Recently the author has found that the NO_3 group is hypsochromous with respect to the neodymium and erbium bands.

Influence of the Solvent.—Theoretically it would be expected that the position of the absorption bands would be different for different solvents. Kundt's rule that the bands should be shifted to the red as the refractive index increases does not hold. It is usually believed that the application of Kundt's rule is obscured by the formation of compounds between the dissolved compound and the solvent. The formation of such solvates seems to be quite definitely proven for some inorganic compounds and organic solvents.[2] Kauffman, Hantzsch and Glover, Gorke, Köppe and Staiger, and others, have recently shown that the extinction coefficient varies somewhat for every solvent. In the same solvent the extinction coefficient usually increases as radicals are added to the dissolved substance so as to increase its molecular weight. Hantzsch[3] gives evidence to show the presence of solvates and molecular aggregates in the case of nitrohydroquinone dimethyl ether.

An interesting investigation has been made by Kalandek.[4] Resonators will emit electromagnetic waves of different wave lengths, depending on the index of refraction of the liquid in which they are vibrating. Kalandek investigated the effect of different solvents on the period of various resonators and also on the positions of the absorption bands of a large number of organic compounds. In general, the relations were

[1] Physic. Rev., Dec., 1909; Feb., 1910.
[2] Anderson: Physic. Rev., **26**, 520 (1908). Jones and Strong: Physik. Z., **10**, 499 (1909); THIS JOURNAL, **45**, 37, 97 (1910).
[3] Ber. d. chem. Ges., **46**, 1556.
[4] Physik. Z., **9**, 128 (1908).

not very close. It would be very interesting, however, to carry these investigations into the infrared.

The Absorption Spectra of Benzene and Its Derivatives.—Benzene and several of its derivatives show selective absorption in the ultraviolet. Generally the absorption spectra of organic compounds consist of very wide diffuse bands. The absorption bands of gaseous benzene, on the other hand, are very fine. Benzene in solution shows seven absorption bands between λ 2330 and λ 2710, and in the gaseous state about 30 bands. Pauer,[1] Friedrichs,[2] Grebe[3] and Hartley[4] have investigated several of the benzene compounds. The bands in the gaseous state are much finer and usually more numerous than in solution or in the solid state.

Both the vapor and solution bands are shifted to the red when the radicals Cl, Br, CH_3, etc., are substituted for hydrogen. The shift is generally greater the greater the molecular weight of the radical. The bands of benzene shifted in this way are the ones that are common to benzene, toluene, ethylbenzene and hydroxyxylene, and are unaffected by temperature and pressure. Hartley gives the following wave lengths for benzene:

	λ.	λ.	λ.	λ.	λ.	λ.	λ.
In sol'n	2682	2657–2642	2614–2600	2539	2480	2426.5	2376
As vapor	2670	2630	2590	2523	2466	2411	2360

As far as investigated, the substitution products of benzene have much less characteristic spectra than that of benzene itself. It would be very interesting to know whether the shift of the bands is gradual as the state is changed or as different chemical radicals are added.

Anthracene has the following bands:

	λ.	λ.	λ.	λ.	λ.
Solid	4250	4495	4745	4980	5300
Solution	4050	4275	4540	4820	....
(Fluorescent) vapor	3900	4150	4320	....	....

The substitution of saturated groups in benzene has been found to change the absorption spectra but little. Unsaturated radicals like NH_2, COOH, etc., change the spectra very greatly, so that there is hardly any relation to the benzene spectra. In the various di-substitution products, the para

[1] Wied. Ann., **61**, 363.
[2] Z. wiss. Phot., **3**, 154 (1905).
[3] *Ibid.*, **3**, 363 (1905).
[4] J. Chem. Soc., **77**, 839 (1900). Phil. Trans., **208**, A, 475–528 (1908).

compounds retain the characteristics of the benzene absorption better than the ortho or meta compounds. A considerable amount of work has been done by Hartley,[1] Baly and Desch,[2] Ley and von Engelhardt,[3] Baly and Collie,[4] Ley,[5] Hartley and Hedley,[6] Baly and Tuck,[7] and others, on the halogen, amino and nitro compounds of benzene, the phenols, pyridine, and its substitution products. Below are a few of the results established:

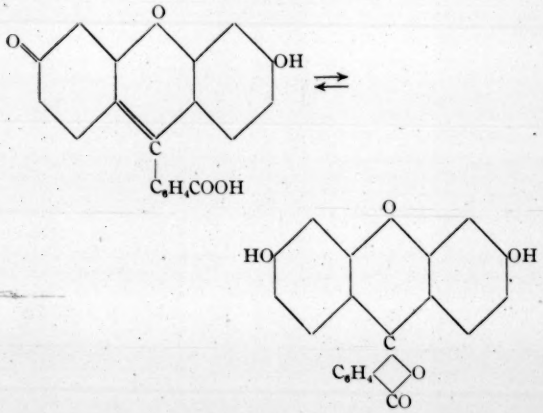
Theory of Dynamic Isomerism.—Baly, Stewart, Desch and others have recently supported the view that the absorption of light by organic compounds does not take place under ordinary conditions, but only when there is a change in the union of the atoms. In some cases this change of union takes place when a chemical compound changes into an isomeric form. Dynamic isomerism takes place when there is some third substance to act as a sort of go-between. Many substances are isodynamic only at high temperatures or in the presence of a catalytic agent. Sometimes the solvent may promote isomeric change. The point of equilibrium is determined by the velocities of the isomeric change, and these velocities are affected by the solvent, concentration, temperature, catalytic reagent, or the presence of free alkalis or acids.

An example of the above change is the transfer of a labile hydrogen atom from an oxygen or sulphur atom to a carbon or nitrogen atom. Sometimes an OH or CN group is transferred in the same way. The atom or radical transferred assumes a neutral condition compared with its condition as a powerful negative radical in the inorganic acids.

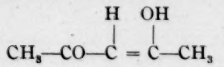
The theory of dynamic isomerism is useful in explaining a large number of phenomena in organic chemistry, and especially those connected with light emission and absorption. Tschugaeff[8] has examined some five hundred compounds for triboluminescence (luminescence due to the crushing of the compound) and has found that 25 per cent. of the organic compounds investigated showed a more or less intense flash when crushed. Most of the luminescent compounds could have existed in several isodynamic forms. Phosphorescence and fluorescence may be explained as being due to a dynamic

[1] Handbuch der Spectroscopie. Vol. III.
[2] J. Chem. Soc., **93**, 1345, 1747, 1902 (1908).
[3] Ber. d. chem. Ges., **41**, 2990.
[4] J. Chem. Soc., **87**, 1344.
[5] Ber. d. chem. Ges., **41**, 1637.
[6] J. Chem. Soc., **91**, 319 (1907).
[7] *Ibid.*, **93**, 1902 (1908).
[8] Ber. d. chem. Ges., **34**, 1820 (1901).

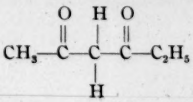
isomerism existing between two or more forms. For instance, fluorescein may exist in two or more forms:



We shall now consider some recent work by Baly and Desch. They first took up acetylacetone, $CH_3—CO—CH_2—CO—CH_3$, and ethyl acetacetate, $CH_3—CO—CH_2—CO_2C_2H_5$, and their metallic derivatives. Acetylacetone and its metal derivatives were found to give similar spectra. Ethyl acetacetate was found to give only a very slight general absorption, whereas its aluminium derivative gave a spectrum almost exactly like that of acetylacetone. Now the work of Perkin and others has shown that free acetylacetone is enolic and ethyl acetacetate ketonic.

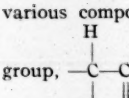
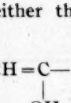


Acetylacetone (enolic).

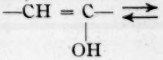


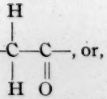
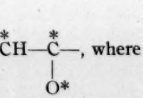
Ethyl acetacetate (ketonic).

These results would then indicate that the metallic derivatives of ethyl acetacetate have the enolic structure, the metal taking the place of hydrogen in the OH group. But by using

various compounds it was shown that neither the ketonic group,  , nor the enolic group,  , give rise to a trace of banded absorption. This would also result from Hartley's work.

It would seem probable, then, that the absorption was not to be attributed to any definite molecular structure but to a dynamic isomerism existing between the two modifications of the compound in solution. Now it was stated before that alkalis and acids change the velocity of the transformation from one form to the other, the final state being unaffected by the catalytic agent. This latter condition means that the direct and reverse actions are equally changed. If now intramolecular change is the source of the absorption bands, then a catalytic agent should affect the persistence of the band. Experimental results verified these conclusions. Other compounds were tried with similar results.

From these results it follows that there must exist, in connection with the reversible transformation of one tautomeric form into the other, a system which is synchronous with the light absorbed. This cannot be a vibration of the labile atom itself, for the oscillation frequency of the absorption bands does not bear any direct relation to the mass of the labile atom and the frequency of atomic motions is never so high as these. The absorption must be due, however, to the oscillation of linking of the keto-enol tautomers: 

 , or, symbolically,  , where the asterisks indicate the points where the migrations of linkages occur. From a summary of work previously done on ultraviolet absorption spectra, it was seen that most of the compounds showing absorption also were tautomeric. As was also seen, an increase of the mass of the molecule in general decreased the oscillation frequency of the absorbed light, although by only a small amount.

Assuming the saturnian form of atom similar to the arrangement assumed by J. J. Thomson, chemical bonds would

simply consist of Faraday tubes of force. Now, by a rearrangement of Faraday tubes, it is quite probable that a vibrational disturbance would be set up. If Hewitt's explanation of the origin of fluorescence is correct, it would follow that disturbances set up by isodynamic changes are of the same frequency as light waves. The luminosity due to thermal or electric action is caused by rapid changes of stress or of the electric action to which the atoms are subjected. Here the disturbances of the electrons are due to the oscillation of linkages within the molecule. The comparatively small displacement of the absorption band by a change in the mass of the molecule is to be expected, for an increase of the mass of matter near a vibrating electron has the effect of retarding its motion, the oscillation frequency becoming less. For instance, the spectral series of Kayser for various related elements show a displacement towards the red on increasing the atomic mass. This is in general true for all emission spectra and for the absorption spectra of the rare earths and organic dyes.

The sodium and aluminium derivatives of ethyl acetacetate show the enolic and ketonic modifications in dynamical equilibrium. The sodium compound is found to be easily decomposed into sodium hydroxide and ethyl acetacetate, whereas the aluminium derivative shows dissociation and hydrolysis to but a very small extent. The absorption spectrum is not dependent on ionization or hydrolysis. Hartley has found that the ultraviolet absorption spectra of metallic nitrates is exhibited even on very great dilution, showing a close connection between the anion and cation in such solutions. Baly and Desch conclude that the Faraday tubes may be lengthened out on dilution and that the force necessary for the separation is furnished by the attraction of the solvent. Solvents which thus exert a strong attracting force are ionizing agents; and this attraction is exerted both on molecules and ions. We have thus hydrated molecules and ions. When the Faraday tubes are lengthened beyond a certain critical value, an interchange of ions between the molecules becomes possible. A completely dissociated solution of a salt is not one in which the ions are moving independently of one another, but one in which the length of the Faraday tubes is greater than the critical value. In tautomeric compounds the Faraday tubes connect the labile atom with the rest of the molecule, being lengthened out to such an extent as to allow these atoms to change their positions in the molecule, and there is a sort of internal ionization within the molecule. To this making and break-

ing of Faraday tubes may be attributed the absorption of the light.

In the tautomeric aliphatic compounds the substitution of an alkyl group for the labile atom destroys the tautomerism. This would be expected, for alkyl ions are unknown. Water and other solvents do not have sufficient attractive force to lengthen out the Faraday tubes in this case. Whether there is a banded absorption in these cases is not stated. One consequence of the theory can be tested. Since the persistence of the absorption band is a measure of the number of molecules undergoing transformation at any moment, this persistence should reach a limit for each tautomeric compound when the length of the Faraday tubes has reached their critical length, so that free interchange takes place. By the successive addition of an accelerating compound a maximum should be found. Experiment shows this to be true. Take the case of ethyl benzoylsuccinate, to which 1, 10, 20, and 100 equivalents of sodium hydroxide have been added. The limits of persistence referred to a 0.0001 normal solution of the ester are as follows:

	Free ester. mm.	1 eq. NaOH. mm.	10 eq. NaOH. mm.	20 eq. NaOH. mm.	100 eq. NaOH. mm.
Absorption band begins at	120.0	63.0	40	31.7	21.9
Absorption band ends at	83.2	34.7	20	15.2	10.4
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Change of dilution over which the band persists	30.7	44.9	50	52.0	52.5

At this point it may be well to refer to the work of Stewart and Baly. Quite a number of chemical facts have been explained by the theory of steric hindrance, although this theory also fails to explain a great many things. For instance, acetic acid, CH_3COOH, is esterified with ease. The methyl, ethyl, etc., derivatives are much more difficult to esterify. This is explained as due to the larger volumes occupied by these radicals and the consequent hindrance to the approach of the alcohol to the carboxyl radical. If, as is probable, however, the intramolecular mean free path is large compared to the size of these radicals, this explanation by steric hindrance breaks down. The theory of isodynamic change will explain all these facts and also others where the theory of steric hindrance would lead to conclusions directly contrary to the facts. According to this theory acetacetic ester exists as

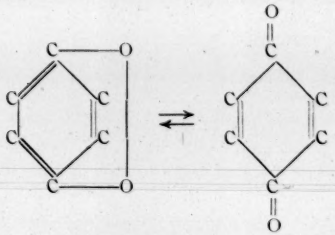
$$CH_3—C(OH)=CH—COOC_2H_5 \rightleftharpoons CH_3—C(=O)—CH(H)—COOC_2H_5.$$

During this dynamic equilibrium there are periods during which a nascent carbonyl group exists. From analogy to the action of other nascent substances, this would occasion a very much greater reactivity.

Stewart and Baly, on further investigation, found that the absorption band in this case has a persistence which decreases proportionately to the decrease of reactivity of the ketone's carbonyl group. It has been noticed by chemists that the velocity of tautomeric change depends on the solvent. Stewart and Baly also found that the persistence of the absorption band was very different in aqueous and alcoholic solutions. In the case of pyruvic ester they show that the facts may be represented by the scheme

$$CH_3—C(=O)—C(=O)—OC_2H_5 \rightleftharpoons CH_3—C(=O)—C(—O)=C—OC_2H_5.$$

In tautomerism we have a wandering of the hydrogen atom, so Stewart and Baly propose to call this process Isorropesis (from the Greek word ἰσορροπεία, equipoise), or an oscillation in the carbonyl grouping. By the persistence of absorption bands it is possible to measure the activity of chemical compounds. The band produced by the isorropesis is also much nearer the red than that produced by the process of enol-keto tautomerism. An example of isorropesis would be the quinone band $1/\lambda = 2480$, which would be due to the following change:



In general, then, according to the theory of Baly, Desch, Stewart and Collie, any absorption by organic compounds is

due to the conditions that occur during isomeric changes. Benzene, for example, appears in two forms and the absorption spectrum is due to a condition of benzene while it is changing from one form to the other. This theory explains quite well the action of chromophores for, as we have seen, every chromophore contains at least one double bond.

Theory of Stark.—Stark[1] considers that chemical valency can be explained as due to the presence of negative electrons that hold the positive parts of atoms together. In Fig. I it is seen how this can take place, the dotted lines representing lines of electric force.

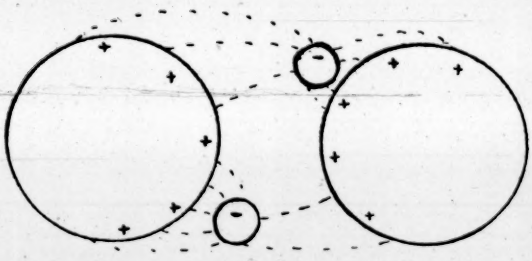


Fig. I.

The conditions represented in Fig. I are such that there is very little stray electric field beyond the atoms. Under such conditions the valency electrons are saturated and Stark represents this by the symbol ←→. Under many conditions, however, the valency electrons are not so closely united to the atoms and are more or less unsaturated. Under certain conditions an electron may be thrown off the atom and Stark considers that it is under some condition such as this that selective absorption of light takes place. When the electron returns to the atom it will undergo certain accelerations along its path and during these accelerations it will emit radiations. Stark believes that under some condition at least similar to this, the fluorescent radiation is emitted and that the period of this radiation will depend on the amount of energy set free when an electron recombines with the positive part of the molecule. From the heat changes which occur in various chemical reactions, Stark calculates what the approximate period of these radiations should be and in many

[1] Physik. Z., **9**, 85 (1908).

cases obtains values which agree with the positions of known bands in the spectrum. Among these bands is the ultra-violet band of benzene. Stark's formula for benzene would be the following:

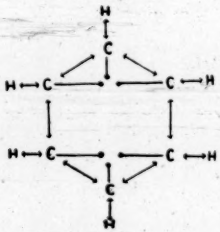
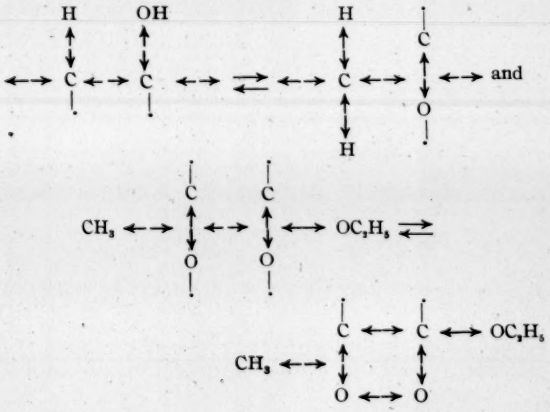


Fig. II.

The symbol —• simply means that one electron is not as closely joined as the other three to the carbon atom. It is possible that even this unsaturated electron may have lines of force running to the other carbon atoms. In this way partial valency can easily be explained. The keto-enolic and isorropesic changes, as interpreted according to Stark's theory, are represented as follows:



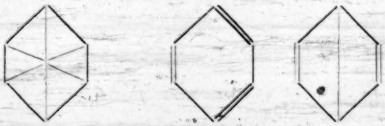
In this consideration of atoms it would be expected in general that the space containing the electric field of the electron would more or less envelop the positive nuclei of the atoms and that the volumes of atoms would depend on their valency. This would agree very well with the assumptions of Barlow and Pope.[1] These assumptions are as follows: In any chemical body the relative volumes of the atoms are proportional to their valencies; in a crystallized body the atoms are close packed; in a compound the volumes of the spheres of atomic influences of atoms of the same valency may differ slightly. The latter variation of the sizes of the spheres of influence (interpreted here as the space filled by the electric fields of the valency electrons) may be due to the different amounts of saturation, or, as Stark calls it, the lack of the valency electrons. It would be interesting to know whether the energy relations support this view, it being expected that the greater the lack of the electrons, the less the potential energy of the compound.

Stark and Steubing[2] have investigated the fluorescence of a large number of organic compounds. Most spectra are banded, and a band never runs in both directions. The band consists of a tail where the smaller bands are close together. From the tail the small bands may run towards the red or towards the ultraviolet, getting farther and farther apart all the time. But there are never small bands on both sides of the tail. The absorption of light by bands running "to the red" is not accompanied by fluorescence or by any photoelectric effects. The absorption of light in bands running towards the violet (benzene bands) is accompanied by a photoelectric effect, a fluorescence of the bands themselves and by a fluorescence of bands due to the connection of carbonyl, ethylene or other chromophoric groups if these be present in the molecule. The addition of more chromophores to the compound shoves the fluorescent bands to the red.

Other Benzene Theories.—There are some color changes of benzene compounds for which the general theory does not seem to account easily. For instance, nitronaphthalene is yellow. By introducing two nitro groups a colorless compound is obtained. In order to explain phenomena of this kind Kauffmann[3] assumes that the introduction of groups into a benzene nucleus may change the condition of the benzene

[1] J. Chem. Soc., **89**, 1675 (1906); **91**, 1150 (1907). Swartz: THIS JOURNAL, **37**, 638 (1907); **42**, 158 (1909).
[2] Physik. Z., **9**, 481, 661 (1908).
[3] Z. physik. Chem., **50**, 530. Ber. d. chem. Ges., **37**, 2941.

ring itself. He considers that benzene may have the diagonal, the Kekulé, or the Dewar[1] formula.



I. II. III.

In condition I benzene has an aliphatic character, as in nitrobenzoic acid, $C_6H_4(NO_2)COOH$. In this condition, having no double bonds, it does not possess strong color properties. The second condition has an aromatic character and is exemplified in the phenols. Examples of the third condition are found in aniline, *p*-phenylenediamine, naphthalene or anthracene. Of the three conditions, the second one is the best chromophore. According to Kauffmann, benzene vapor exists in the diagonal condition and for that reason it is not luminous when exposed to electric discharges of high frequency or to the rays from radium. Auxochromes and chromophores cause the benzene to become luminous and for this and other reasons Kauffmann thinks that the condition of the benzene grouping has been changed.

The different changes in color may be due to one or more of three conditions:

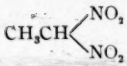
1. There may be no intramolecular changes of constitution, but the whole change of color may be due to the change in the radicals.

2. There may be an intramolecular rearrangement.

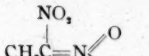
3. There may be an association of the molecules or compounds formed with the solvent. The above classification includes color changes that are not explained by isomerism.

In many cases it is practically impossible to decide between the different possibilities. Auwers[2] and Tuck[3] give evidence to show that the sodium salt of hydroxyazobenzene owes its color simply to the introduction of the sodium. Baly and Schaefer,[4] Hantzsch,[5] Vey, Gorke,[6] and others, give some cases coming under class 2. As example, we may take dinitroethane:

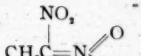
[1] Ber. d. chem. Ges., **33,** 1725; **34,** 682; **35,** 3668. Z. physik. Chem., **55,** 547.
[2] Ann. Chem. (Liebig), **360,** 11.
[3] J. Chem. Soc., **91,** 454 (1907).
[4] *Ibid.*, **93,** 1806.
[5] Hantzsch: Ber. d. chem. Ges., **32,** 575. Hantzsch and Veit: *Ibid.*, **33,** 626. Ley and Hantzsch: *Ibid.*, **39,** 3149.
[6] Hantzsch and Gorke: *Ibid.*, **39,** 1073.



Pseudo acid, colorless.

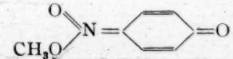


Sodium salt, yellow.



Acid, yellow.

Nitrophenol ether, faintly yellow. Benzene derivative.



Chloronitrophenol ether, deep red. Quinone derivative.

A very full discussion of the "Umlagerung" theory is given by Ley.[1] A short discussion is also given of the theory of indicators, of polymerization, and of metallic derivatives of organic compounds, especially of cases where the metal is supposed to be present in the inner part of the molecular complex.

W. W. STRONG.

REVIEWS.

COLLOIDS AND THE ULTRAMICROSCOPE. A Manual of Colloid Chemistry and Ultramicroscopy. By DR. RICHARD ZSIGMONDY, Professor of Inorganic Chemistry in the University of Göttingen. Authorized Translation by JEROME ALEXANDER, M.Sc. With Two Colored Plates and Numerous Illustrations. New York: John Wiley & Sons; London: Chapman & Hall, Ltd. 1909. pp. xiii + 245.

An interesting treatment of the modern theory of colloidal solutions and suspensions, their physical and chemical properties, and the use of the ultramicroscope in their study. The ultramicroscope as developed by Siedentopf and Zsigmondy is merely the old device of oblique illumination pushed to the extreme limit. The powerful beam of light, traversing the fluid in a horizontal direction, is diffracted or scattered by the minute particles, and this light, entering the microscope, makes the particles visible as minute specks of light on a black background. A very complete exposition of this method for studying the movement (Brownian), size and distribution of the particles in suspension is given. Five chapters are devoted to colloidal gold alone, and there is much valuable information regarding the nature of jellies and gelatinous substances, hydrosols, colloidal sulphides, etc.

The book makes interesting reading for the chemist and physical chemist, although it is not as well arranged as it might be, and there are some repetitions. The pros and cons for and against various theories, by various writers and ex-

[1] Jahrb. d. Rad. u. Elek., **6**, 341, 381 (1909).

perimenters, are so well mixed together that the reader is often in doubt about which to accept. R. W. W.

THE MODERN ASPHALT PAVEMENT. By CLIFFORD RICHARDSON, M. Am. Soc. C. E. Second Edition. New York: John Wiley & Sons; London: Chapman & Hall, Ltd. 1908. pp. ix + 629.

A more comprehensive and valuable work on this subject is hard to find. The author is of ripe experience and deeply rounded in his subject and has established successfully a reputation as an expert chemical engineer. The natural tendency, so frequently manifested by technical writers, to indulge too freely, for the convenience of the average reader, in professional language has apparently been carefully avoided and the book, without being unnecessarily verbose, is clear to the layman and to the professional. In matters of professional judgment, there always will be differences of opinion between experts, but the clear and positive expression of the judgment of one will always be of value to the others, whether or not they wholly agree. Both the statements of facts and of opinions in this work are clear and positive and generally as concise as proper consideration for the wide class of readers for which the book is intended will allow.

The subject is treated exhaustively. Very little of value seems to have been omitted and the book seems as nearly up to date as it is possible to expect, especially in view of the almost daily changes and discoveries being made in the subject under discussion.

The work is admirably arranged as to sequence of topics and an appreciable convenience is the "Summary" printed after each chapter, which gives briefly a description or the conclusions of the discussion of the chapter. The book is, in the judgment of the reviewer, well suited for use as a text-book in an engineering course and most valuable for reference to any one connected with the work it covers.

In accepting the statements of opinion or judgment made by the author, it, of course, should be remembered that the latter has been for many years, and we understand still is, employed by a concern deeply interested in the use of asphalt from a particular source. The impressions he has received through the media of his surroundings may, therefore, have been somewhat tinged in passing through the same, and it is possible that this explains some differences of opinion or judgment that, in spite of the undoubted effort of the author to be fair and impartial, exist between himself and others who have been differently situated. The book in its appearance reflects great credit on its publishers. W. B. C.

PHYSICAL CHEMISTRY FOR ELECTRICAL ENGINEERS. By J. LIVINGSTON R. MORGAN, PH.D., Professor of Physical Chemisty in Columbia University. Second edition, revised. New York: John Wiley & Sons; London: Chapman & Hall, Ltd. 1909. pp. x + 249. Price, $1.50.

The object of this work is to give "a knowledge of physical chemistry sufficient in scope for the understanding of current work in electro-chemistry." The book is divided into eight chapters, which treat respectively of atomic and molecular weights, of the properties of gases, the first and second laws of thermodynamics, solutions, chemical mechanics, equilibrium in electrolytes and electrochemistry. The final chapter consists of a set of problems with answers. The subject is placed on an experimental basis by discarding all hypothesis and by keeping before the reader's mind the experimental facts on which his ideas are based. The general method of treatment is clear and calls for no further special comment. One or two points that might be improved on may be mentioned. It is stated on p. 126 that to integrate the van't Hoff equation q must be considered independent of the temperature. This is not correct, as it may be integrated if q is a known function of the temperature.

The discussion of the decomposition of water is rather out of date, as it is now known that if the potential of oxygen could be measured it would be 1.22 volts against hydrogen, and that whatever the value 1.07 may mean, it is not the potential of the hydrogen-oxygen cell.

The problems cover all the matter contained in the text and are a valuable addition to the book. It is unfortunate, however, that more attention has not been paid to the proper use of insignificant figures, as for example in problem 56, where the data are given to two places and the answer is worked out to five.

These points, however, do not materially alter the value of the book to the beginner, to whom it may be safely recommended.

M. DEKAY THOMPSON.

A TEXT-BOOK OF PHYSICAL CHEMISTRY THEORY AND PRACTICE. By ARTHUR W. EWELL, PH.D., Asst. Professor of Physics, Worcester Polytechnic Institute. Philadelphia: P. Blakiston's Son & Co. 1909. pp. vii + 370. Price, $2.25.

This book is a new departure as a text-book of physical chemistry, being "intended to serve as a laboratory manual, as a text-book to accompany recitations or lectures, and as a convenient book of reference," all in one. It bears very plainly the stamp of a teacher of physics. The usual aim of a course in physical chemistry is to equip prospective chemists with all the possible means of attacking their problems.

There are probably few teachers, therefore, who would consider it wise to follow this author and spend time on such things as the hygrometer, the measurement of the angle of a prism, of the velocity of sound and of the wave length of light, while giving but ten lines to colloidal solutions, two lines only of actual information about catalysis, nothing about mixed crystals, the real cause of hydrolysis, or association as indicated by surface tension.

There are several misleading statements. The modern "normal weight" of cane sugar does *not* produce the same rotation as 1 mm. of quartz, as stated on page 223. On page 272 we read of a "mixture (solid solution) of solid silver and solid eutectic alloy," a new definition of solid solution. The mercury still pictured on page 74 is antiquated since the work of Hulett.

The publishers' and proof-readers' work has been well done, though it is surprising to see a cut inverted on page 93. The text is clear, concise and well arranged. The experiments are interesting and suggestive, as the author has not given the usual miniature Ostwald-Luther. Since most teachers doubtless prefer to arrange their own course, the physical standpoint will not prevent the book from being a useful addition to their libraries.

JOEL H. HILDEBRAND.

PHYSIKALISCH-CHEMISCHE RECHENAUFGABEN. Von DR. R. ABEGG, Professor, und DR. O. SACKUR, Privatdozent, an der Universität Breslau. Leipzig: G. J. Göschen'sche Verlagshandlung. 1909. pp. 104. M. 0.80.

As the title implies, the booklet is a series of values and equations that are frequently used in physical-chemical calculations.

H. C. J.

CHEMICAL CONVERSION TABLES, for Use in the Analysis of Fertilizers, Fertilizing Materials, Iron and Its Products, Etc., Etc. By H. B. BATTLE, PH.D., and W. J. GASCOYNE, PH.D., Baltimore: Williams & Wilkins Pub. Co. 1909. pp. 79. Price, $2.50.

Tables are given for phosphoric acid, potash, ammonia and protein, nitrogen, chlorine, sulphur, alumina, phosphorus and magnesia, silica, and manganese. The weight of precipitate obtained from 1 or 0.5 gram of sample is given to 0.1 milligram and the corresponding percentage of the substance sought to 0.01 per cent. The tables are clear and conveniently arranged. The book is designed for use in commercial laboratories and will prove a great time-saver for those who handle many analyses involving these substances. It is durably and elegantly bound in leather.

E. EMMET REID.

ELEMENTARY CHEMISTRY. By HOLLIS GODFREY, Head of the Department of Science, Girls' High School of Practical Arts, Boston, Mass. New York, London, Bombay and Calcutta: Longmans, Green & Co. 1909. pp. xiv + 456.

In contents this book, apparently intended for schools, differs from the average first-year college manual only in the omission of some of the rarer elements and compounds. The dissociation theory is introduced, technical processes are well described and illustrated, and the book requires as much work and intelligence on the student's part as most college books.

It differs from other books in its profuse illustrations and in the author's style. The illustrations are technically very fine and include apparatus, technical processes and portraits, while some of the pictures may be considered as art for art's sake. For example, a picture of a very fine ripe apple illustrates the statement underneath: "Unripe fruit is acid; the ripened fruit sweet because of the addition of sugar." An artistic picture of high waves at sea illustrates the fact that there is salt in sea water. As to the author's style a single quotation must suffice, for his rhetorical periods are lengthy. Bear in mind that this book is not a primer but is full of chemical fact calling for close study but adorned every few pages with a flight like the following on Avogadro's hypothesis:

"It was about a century ago that the Italian scientist, Avogadro, proposed this wonderfully simple yet daring theory. Briefly stated, it is as follows: 'The same number of molecules may be found in equal volumes of all gases which have the same temperature and pressure.' Think of two old deserted barns of exactly the same size, which stand on either side of some old country road. Suppose both barns are filled with barn swallows, with swallows sweeping to the eaves across the hay, by the old stalls, and through the harness room. Each barn would be filled with ever-moving life whose sum would be the sum of all the swallows in the barn. Change from the two barns full of swallows to two jars full of gases. A liter of chlorine gas standing beside a liter of hydrogen gas is in our belief filled with moving life. The molecules which constitute the matter of the gas are in constant motion, bounding and vibrating to and fro within the confines of the vapor. There are so many in even a liter of gas that our finite minds can scarcely imagine their number. Think, then, what a wonderful imagination a man must have had to conceive that every liter or other fixed volume of a gas contains exactly the same number of these tiny bodies."

This simile, as stated, may illustrate the kinetic theory

of gases; it does not illustrate Avogadro's law, unless swallows obey the gas laws which the author does not state in his description of the barns.

The author is not only sometimes vague in his rhetoric but is inaccurate in some statements. On page 154, in speaking of the Birkeland-Eyde process, he says: "The rushing air meets the terrific temperature of the electric flame, and a portion of its nitrogen is combined with the accompanying oxygen with production of various oxides of nitrogen, particularly nitrogen pentoxide." As a matter of fact, the only oxide of nitrogen stable enough to exist even momentarily under the working conditions is nitric oxide, and the work of completely transforming the nitric oxide to nitrogen dioxide and thence to nitric acid is carried on in the acid towers. On page 252, in speaking of Moissan's diamonds, the author says: "The jewels found were small and of various colors; only a few were white, so the cost of the process was much more than the value of the thing obtained." This gives a misleading impression. The author should have stated the crude fact that the largest of Moissan's diamonds was 0.5 mm. in diameter, and the total output commercially valueless.

It is an ungracious duty to review a conscientiously written book unfavorably, and it must be borne in mind that the book may impress others quite differently. It must be granted that if it is really true, as the author evidently believes, that long rhetorical introductions and similes help and do not repel intelligent girls in studying chemistry, and that this sugar-coating induces them to assimilate chemical theory and fact, then this is an exceptionally good text-book. E. R.

AN ELEMENTARY TREATISE ON QUALITATIVE CHEMICAL ANALYSIS. By J. F. SELLERS, Professor of Chemistry in Mercer University, Macon, Ga. Second Revised Edition, with Notes and Tables. Ginn & Co. 1909. pp. 176. Price, $1.00.

The distinctive features in this book are the chapters on the theory of analytical operations admirably written from the standpoint of electrolytic dissociation, and the chapter on analytic separations with theory and examples for practice. The author simply and clearly emphasizes by questions, answers and examples the application of the dissociation theory. The methods of separation used are good. E. R.